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CHROME-MAGNESITE BRICK FOR OPEN-HEARTH FURNACES*

By J. H. Chesters† and T. R. Lynam‡

Abstract

(1) The attempt to replace silica brick in open-hearth furnaces by more refractory basic brick has raised a number of interesting problems. Thus, chrome-magnesite brick, although much improved in their physical properties, are subject to certain limitations in service, *e.g.*, the bursting which occurs when they become impregnated with iron oxide. (2) The properties of a number of British and Continental chrome-magnesite brick are given, including data on the factors determining their thermal-shock and bursting resistance. The influence of iron oxide on the melting point of chrome-magnesite brick is also discussed. (3) The results obtained, both with limited trials and with complete furnaces built from chrome-magnesite brick, are described, and an attempt is made to analyze the ultimate causes of failure. (4) Both laboratory and service tests suggest that the bursting which accompanies iron-oxide absorption is responsible for a considerable part of the damage but that this can be overcome at least in part by a modification of the brick batch. With hot metal furnaces, where the concentration of iron oxide is lower and shutdowns less frequent than in cold metal furnaces, the life obtained with chrome-magnesite brick is considerably greater.

I. Introduction

Chemical analyses of brick removed from basic open-hearth furnaces show that iron oxide and lime are the principal materials attacking the brickwork above the bath level. Those parts of the back and front walls in a stationary furnace that are close to the bath become splashed with slag; farther up, the silica content of the slagged brick is often lower than that of similar brick before use. From the standpoint of slag attack, therefore, such furnaces logically should be constructed of basic refractories which possess, in addition to far greater resistance to chemical attack by iron oxide and lime, a much higher refractoriness. Numerous attempts have been made to achieve this object, but it is only comparatively recently that "all-basic furnaces" have been constructed that have lasted long enough to give promise of an overall saving.

The success of silica, in spite of its small safety margin as to refractoriness, would appear to be due to its excellent physical properties; in particular to its freedom from after-shrinkage and its ability to carry a relatively high load to within a few degrees of its melting point. Attempts to replace silica by magnesite usually result in structural spalling, while chrome-magnesite brick swell because of iron-oxide absorption and break off long before they have been slagged away. During the last few years, special chrome-magnesite brick of high thermal-shock resistance and high refractoriness under load have been developed that show more promise. Further research is required before such brick can hope to replace silica in the roofs of open-hearth furnaces, but progress will continue to be rapid inasmuch as the field is relatively new and there is still much to be understood regarding the reactions involved. In view of these facts, it may only be a matter of a few years before the "all-basic furnace becomes a practical proposition. The problem is an important one because, if it is solved, greater outputs will be obtained from existing furnaces, and higher operating temperatures will be possible.

II. Properties of Commercial Chrome-Magnesite Brick

The properties of the principal chrome-magnesite brick used in Great Britain are summarized in Table I. They vary between fairly wide limits. Brick (A), (B), (C), and (F) have given good service in the back and front walls of basic open-hearth furnaces; brick (E) and (H) have given less satisfactory results. Brick (E), which has a low thermal-shock resistance, has given trouble due to cracking, and (H), which has a low refractoriness under load, has given trouble due to softening and collapse. Brick (D) and (G) are still undergoing tests, and it is too early to express an opinion as to their durability.

The brick which have given outstanding service have all shown a high thermal-shock resistance in the test which is described in this paper. The writers do not suggest that *any* chrome-magnesite brick with a high thermal-shock resistance will be durable, but if a brick is to undergo the numerous week-end shutdowns associated with a long campaign on a cold metal furnace, it must possess at least a moderate amount of thermal-shock resistance.

The ultimate cause of failure is the bursting of the brickwork caused by the absorption of iron oxide. Details of the mechanism of bursting and of laboratory simulative tests will be given later, but it can be stated that the brick which are giving the best service have a relatively low bursting expansion in the laboratory test.

Abnormally high refractoriness under load does not appear to be an essential property of front- and back-wall brick. Good service has been obtained with chrome-magnesite brick, $3^1/_2$ by 2 by 2 inches, test

* Presented at the Fortieth Annual Meeting, American Ceramic Society, New Orleans, La., March 30, 1938 (Refractories Division). Received March 31, 1938.

† Central Research Department, United Steel Companies, Ltd., Stocksbridge, near Sheffield, England.

‡ The Oughtibridge Silica Firebrick Co., Ltd., Oughtibridge, near Sheffield, England.

TABLE I

PROPERTIES OF COMMERCIAL CHROME-MAGNESITE BRICK

	Chrome-magnesite brick (A)	(B)	(C)	(D)	(E)	(F)	(G)	(H)	Range
Approx. chrome-to-magnesite ratio	75/25	75/25	75/25	75/25	75/25	60/40	75/25	90/10	60/40–90/10
Porosity (%)	26.2	26.1	26.0	19.4	29.3	21.2	22.6	28.4	19.4–29.3
Bulk density (c.g.s. units)	2.89	2.83	2.90	3.18	2.68	3.00	3.04	2.84	2.68–3.18
Specific gravity	3.91	3.83	3.90	3.93	3.86	3.81	3.92	3.97	3.81–3.97
Crushing strength (lb./sq. in.)	1140	1050	2120	3540	Not done	3660	1590	2840	1050–3660
Permeability to air (perpendicular to 9 by 3 in. through 1 skin) (c.g.s. units)	0.430	0.055	0.030	0.020	0.154	0.016	0.211	0.175	0.016–0.430
After-shrinkage or expansion (%) (2 hr. at 1500°C)	0.5 (exp.)	Not done	0.3 (exp.)	0.0	1.3 (exp.)	0.1 (exp.)	0.3 (exp.)	0.2 (shrink.)	−0.2–+1.3
Refractoriness under load (50 lb./sq. in.)									
Initial softening (°C)	1470	1400	1400		1420	1430	1380	1300	1300–1470
Rapid softening (°C)	1600	1490	1520		1500	1590	1520	1350	1350–1600
Fail temperature (°C)	1660	1570	1705	1740	1560	1650	1600	1380	1380–1740
Thermal-shock resistance (av.)	30+	30+	30+	30+	4	*28+	30+	10	4–30+
Bursting expansion (%)	17.2	12.1	26.3	12.1	51.4	17.4	39.0	42.4	12.1–51.4
Chemical analysis (%)									
SiO_2	7.9		6.5	5.2	9.3	4.6		8.5	4.6–9.3
Fe_2O_3	9.2		11.2	11.7	12.5	12.9		21.4	9.2–21.4
Al_2O_3	12.9	Not done	7.2	9.9	6.8	13.4	Not done	11.1	6.8–13.4
Cr_2O_3	32.1		35.1	32.7	30.3	20.9		36.7	20.9–36.7
MgO	37.8		38.9	39.1	39.8	45.5		19.0	19.0–45.5

* Average of 26 and 30+.

pieces from which failed at 1560° C when heated up at 10°C per minute under a load of 50 lb. per sq. in. This was probably due to the fact that the dead load in these positions was quite low and that in any case only the front part of the brick reached such high temperatures.

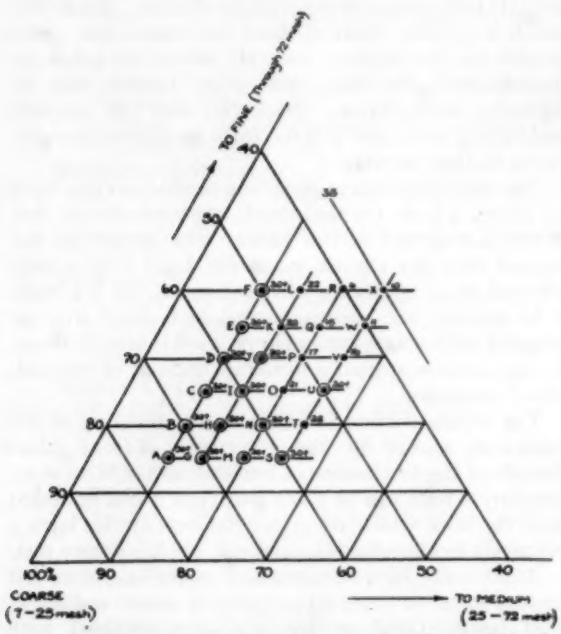

FIG. 1.—Influence of grading on the thermal-shock resistance of 75 to 25 chrome-magnesite brick.

III. Laboratory Development Work

(1) Thermal-Shock Resistance

The grading of a refractory often has a considerable influence on its spalling resistance. With this in mind, a large number of 75 to 25 chrome-magnesite test pieces, 3 by 2 by 2 inches, were made, and their thermal-shock resistance was determined. The test employed, which has already been described,[1] may be summarized as follows: The test pieces are placed in a furnace maintained at 900°C. After ten minutes they are removed and set on end on a 3-in. thick fireclay brick floor; after ten minutes, they are again placed in the furnace. This process is repeated until the test piece can be pulled apart in the hands. The thermal-shock resistance is defined as the number of such reversals required to produce failure. The method does not attempt to simulate service conditions. It *does* give an idea of the thermal-shock resistance of the material, just as after-shrinkage tests indicate volume stability at high temperatures. Results obtained over a wide range of refractories show a remarkable degree of correlation with the results obtained in service.

The gradings employed and the thermal-shock data obtained are given in Table II and Fig. 1. The highest thermal-shock resistance was shown by the coarser mixtures. An increase in the percentage of fine (and to

[1] J. H. Chesters and L. Lee, "Properties of Magnesite and Chrome-Magnesite Brick," *Trans. Ceram. Soc.* [England], **36** [7] 294–310 (1937); *Ceram. Abs.*, **17** [3] 105 (1938).

TABLE II

INFLUENCE OF GRADING ON THERMAL-SHOCK RESISTANCE

Grading: B.S.I. sieves

	7- to 25-mesh (2.41–0.60 mm.)	25- to 72-mesh (0.60–0.21 mm.)		Through 72-mesh (< 0.21 mm.)		
Index	Chrome (A)(%)	Chrome (A) (%)	Magnesite (A) (%)	Chrome (A) (%)	Magnesite (A) (%)	Thermal-shock resistance
(A)	75		10		15	30+
(B)	70	5	5		20	30+
(C)	65	10			25	30+
(D)	60	10		5	25	30+
(E)	55	10		10	25	30+
(F)	50	10		15	25	30+
(G)	70	5	10		15	30+
(H)	65	10	5		20	30+
(I)	60	15			25	30+
(J)	55	15		5	25	30+
(K)	50	15		10	25	20
(L)	45	15		15	25	22
(M)	65	10	10		15	30+
(N)	60	15	5		20	30+
(O)	55	20			25	21
(P)	50	20		5	25	17
(Q)	45	20		10	25	15
(R)	40	20		15	25	6
(S)	60	15	10		15	30+
(T)	55	20	5		20	28
(U)	50	25			25	30+
(V)	45	25		5	25	16
(W)	40	25		10	25	11
(X)	35	25		15	25	10

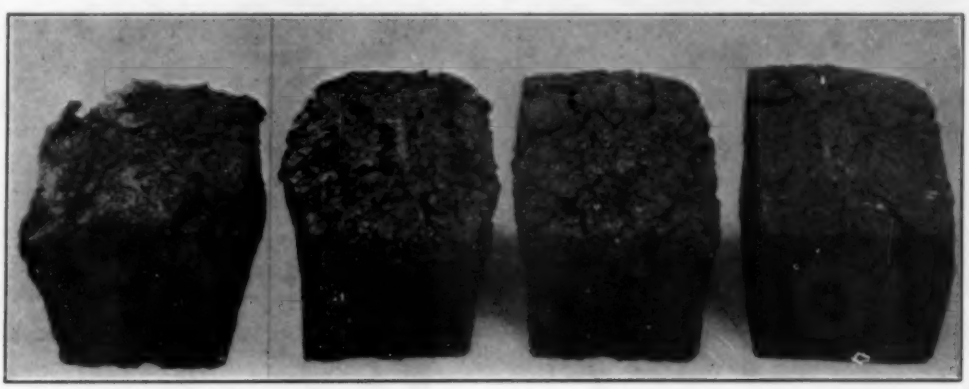

FIG. 2.—Chrome-magnesite brick test pieces burst with iron oxide.

a less extent of medium) material resulted in much lower thermal-shock resistance.[2]

Figure 1 shows how important it is to control the grading of a chrome-magnesite batch if high thermal-shock resistance is desired. Sieving and re-mixing are almost essential because the rate of grinding varies greatly with the chrome ore used, and serious variations in the grading will occur unless frequent checking is employed.

[2] Chrome-magnesite brick gradings falling within this high thermal-shock area were used in earlier experiments by Lynam and Rees. See T. R. Lynam and W. J. Rees, "Mixtures of Chromite and Grecian Magnesite, I–II," reprinted in *Trans. Ceram. Soc.* [England], **36** [3] 137–72 (1937); *Ceram. Abs.*, **16** [10] 304 (1937).

The chemical analyses of the raw materials and the grading of the "through 72-mesh" sections are as follows:

B.S.I. sieves	Chrome (A)(%)	Magnesite (A)(%)
72- to 150-mesh (0.21–0.10 mm.)	59	17
Through 150-mesh (< 0.10 mm.)	41	83
Analysis		
SiO_2	1.4	2.1
Fe_2O_3	17.2	3.1
Al_2O_3	12.6	2.3
MgO	16.1	91.9
Cr_2O_3	50.9	

Brick made from magnesite or chromite alone, using a grading, such as (M), which with a 75 to 25 chrome-magnesite brick yields a high thermal-shock resistance,

fail after only a few reversals. This difference may be due in part to the formation in the chrome-magnesite brick of a crystalline bond, but this would not explain why a particular grading, such as (M), gives better thermal-shock resistance than a much finer grading, such as (R).[3] Chrome and chrome-magnesite test pieces of known thermal-shock resistance have been made, and their modulus of rigidity and shearing strength at various temperatures are being determined.

The length and breadth of the chrome-magnesite test pieces at the top and bottom (when lying on a a 3- by 2-inch face) and the height were then measured by sliding calipers. The test pieces were set on magnesite brick in a gas-fired kiln, and the mill-scale pills were placed centrally on top of the test pieces with their long axes parallel to their length. The temperature of the kiln was raised to 1600°C in about three hours, and this temperature was maintained for one hour.

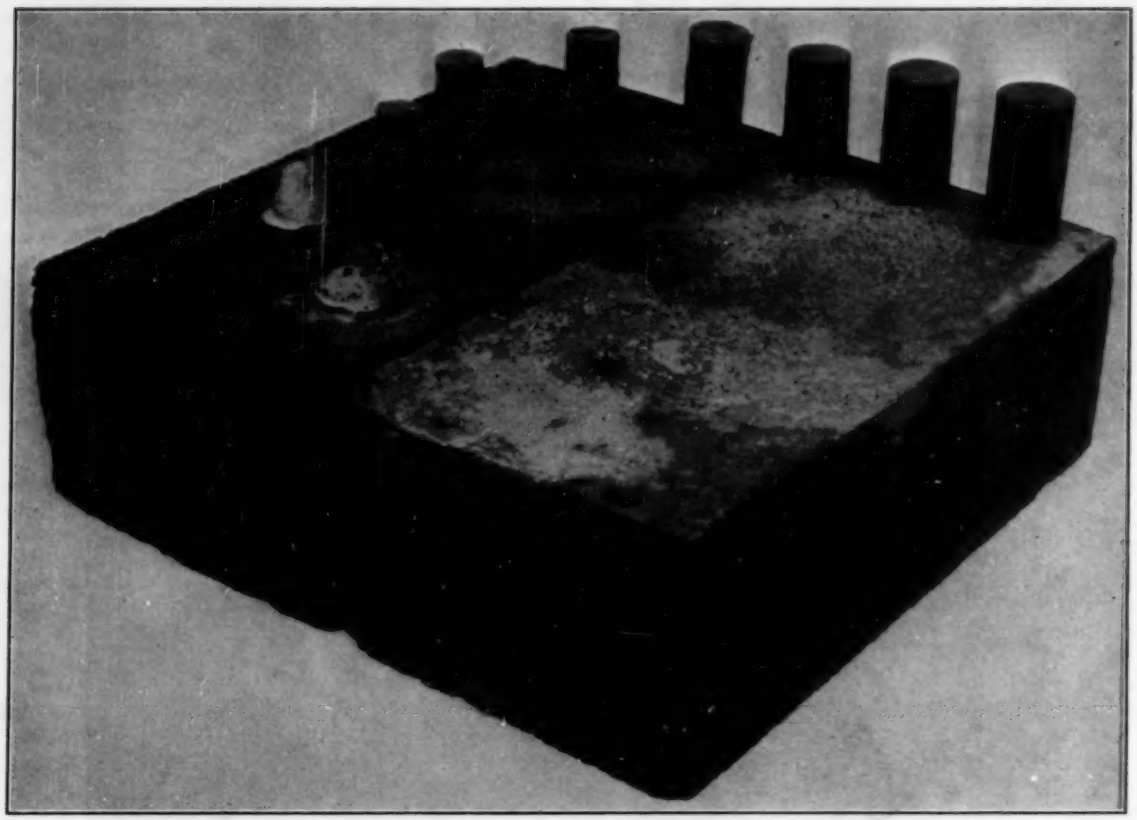

FIG. 3.—Influence of iron oxide on the melting point of chrome-magnesite brick; *right to left*, chrome-magnesite-FeO (equivalent) mixtures, 100–0, 90–10, 80–20, etc.

(2) Bursting Expansion in Presence of Iron Oxide

The bursting of chrome-magnesite brick in open-hearth furnaces has been simulated in the laboratory by the following test:

Test pieces, 3 by 2 by 2 inches, were molded from mixtures of known composition and were fired or cut from a test brick. Cylindrical pills, about $2^1/_2$ by $^3/_4$ inches, were molded of mill scale using sulfite lye as a bond. The analysis of the scale used was as follows:

	(%)		(%)
Fe_2O_3	49.5	Mn	0.4
FeO	47.2	Si	0.9
Fe	0.3	S	0.1
C	1.4		

[3] An attempt is being made to answer these questions by elasticity measurements which Professor Cobb and Dr. Roberts of the University of Leeds have undertaken to carry out.

Upon cooling, the test pieces were again measured, and the percentage expansion of the length and breadth of the top face and of the height were added together. In this way, bursting expansion figures, such as those given in Table I, were obtained. Figure 2 illustrates the expansion obtained.

The bursting expansion, unlike the thermal-shock resistance, is found to be almost independent of the grading employed. Thus with the mixtures (H), (J), and (L), referred to in Table II, the following results were obtained:

	Grading (%)			Bursting expansion (%)
	(coarse)	(medium)	(fine)	
(H)	65	15	20	31.2
(J)	55	15	30	34.0
(L)	45	15	40	31.3

The principal factors controlling the bursting expansion appear to be the chrome-to-magnesite ratio and the nature of the chrome ore used. Whether the low bursting expansions obtained with certain chrome ores are due to the chromite itself or to the amount of secondary constituent present is not yet clear.

(3) Thermal-Shock Resistance of Slagged Samples

It has been found possible to produce chrome-magnesite brick with a high initial thermal-shock resistance and a relatively low bursting expansion. The question arises, however, as to whether brick which contain an abnormally high amount of serpentine in the chrome ore and have a low bursting expansion will be sensitive to thermal shock after having been in contact with iron oxide. With this in mind, a number of thermal-shock tests has been made on chrome-magnesite test pieces after use in the bursting test. Certain of the test pieces, *e.g.*, mixture (H) in Table II,

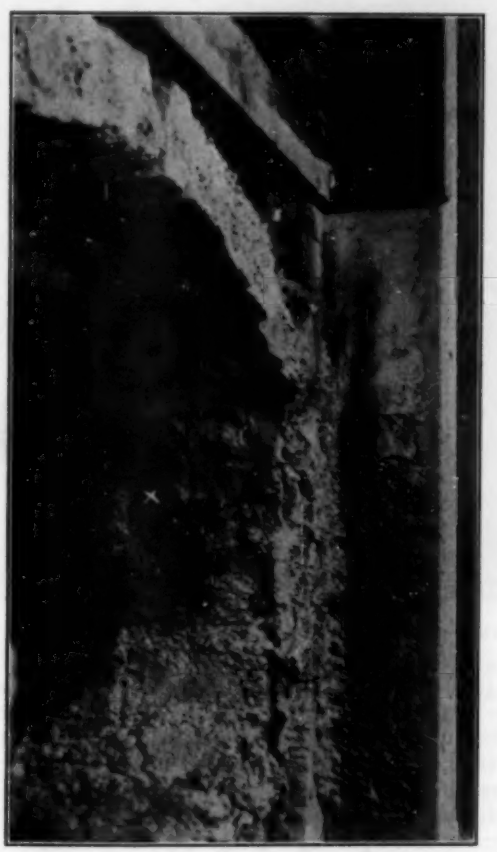

FIG. 4.—Bursting of chrome-magnesite brick in front wall of open-hearth furnace; note gap between split surface and remainder of the brickwork.

still gave thirty reversals, but others, to which additions had been made to reduce bursting, showed a markedly lower thermal-shock resistance after the bursting test. These results suggest that, in the development of chrome-magnesite brick, it may be necessary to compromise between low bursting expansion and high thermal-shock resistance after contact with iron oxide.

(4) Influence of Iron Oxide on the Melting Point of Chrome-Magnesite Brick

The high safety factor of chrome-magnesite brick when brought in contact with iron oxide at open-hearth furnace temperatures is shown by the melting points of pills made from chrome-magnesite brick–iron-oxide mixtures.

FIG. 5.—Chrome-magnesite brick in downtake after 560 casts.

The iron was added as ferrous oxalate, and the pills were heated on a magnesite brick in a gas-fired kiln.

Chrome-magnesite brick (%)	Iron oxide (calculated as FeO) (%)	Collapse point of pill (°C)
0	100	1470*
10	90	1550
20	80	1580
30	70	1660
40	60	Over 1660
50	50	" "
60	40	" "
70	30	" "
80	20	" "
90	10	" "
100	0	" "

* The high melting point is due to oxidation of the FeO.

Figure 3 shows the state of the pills after heating to 1660°C.

IV. Open-Hearth Furnace Trials

(1) All-Basic Furnace

During the last few years, a number of all-basic furnaces have been built in Great Britain. All of the brick used above the stage level, except the fireclay door brick, were of the basic type. The main roof,

ramps, ports, and uptakes were built of special chrome-magnesite brick. The lives obtained with such furnaces have been rather disappointing to the practical man, but to the research worker they are encouraging because they represent a big step in the direction of the ideal of an all-basic furnace.

Two furnaces, both of the cold metal stationary type and of about 70 tons capacity, have been followed closely. The first ran for 357 casts after which it had to be rebuilt; the second lasted 560 casts, but it required a major roof repair after 288 casts.

Hot metal furnaces constructed from similar materials are giving more promising results. This is presumably due to the low concentration of iron-oxide possibility for roofs, its use is already practical for side walls in certain basic open-hearth furnaces. In tilting-furnace back walls, magnesite and special chrome-magnesite brick have given equal service.

Brick (A), (B), and (F) have given a life of about eleven to thirteen weeks in back walls as compared to four weeks with the combination of silica and chrome brick previously used. This performance represents a considerable economy, even if no allowance be made for the labor saved and the reduction in strain on the roof due to the less frequent replacement of back and front walls. The used brick are still highly refractory and can be employed in other constructions or as refractory cement.

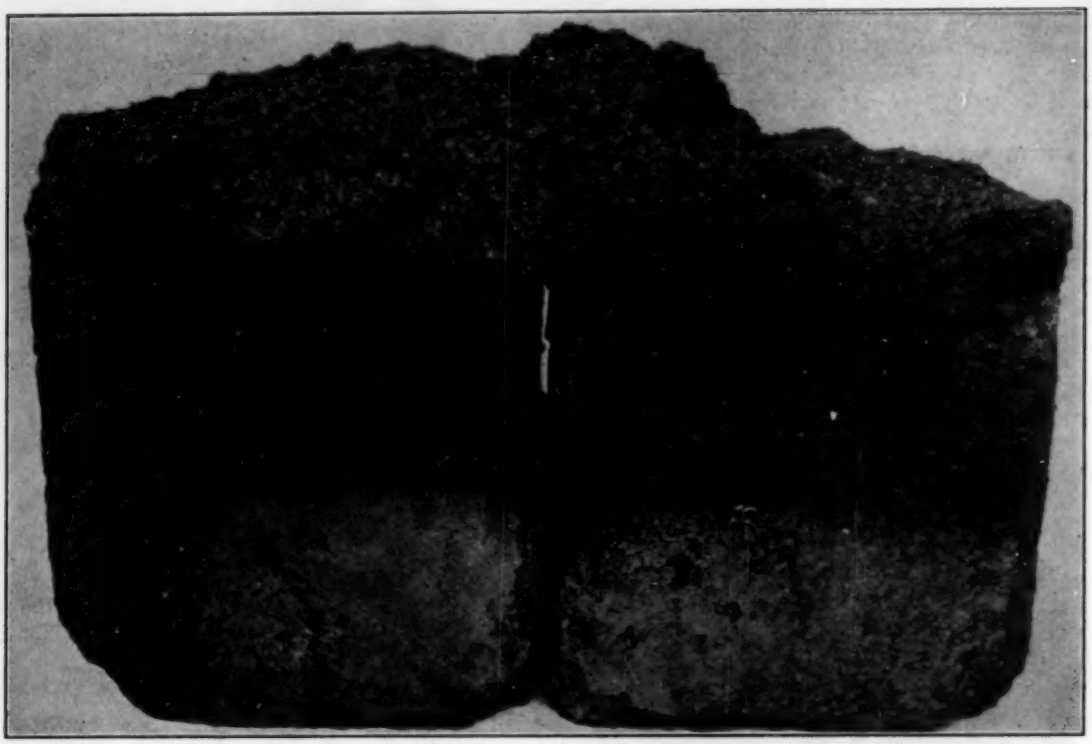

FIG. 6.—Chrome-magnesite brick after $11\frac{1}{2}$ weeks in back wall; original thickness, 9 in.; final thickness, $5\frac{1}{2}$ in.

vapor in such furnaces compared with that found in cold metal furnaces melting light scrap and to the absence of week-end shutdowns. The latter might not appear to be a matter of importance where a furnace is constructed of brick with a high thermal-shock resistance, but it should be pointed out that this resistance decreases considerably in service and that, in any case, large pieces of brick, which have burst away from the roof and side walls but have not yet actually become detached, are likely to come away during these shutdown periods.

(*a*) *Back- and Front-Wall Trials:* Numerous trials of chrome-magnesite brick have been made in the back and front walls of stationary furnaces. The results suggest that even if the chrome-magnesite brick requires improvement before becoming an economic

(*b*) *Ports:* The behavior of chrome-magnesite brick in ports still leaves a good deal to be desired. Their use permits a shorter port with a consequent increase in furnace output, but after a few weeks of service they tend to soften and distort. Whether this softening is due to the relatively low initial strength of chrome-magnesite brick at high temperatures or to iron-oxide absorption can not be yet stated with any certainty; here again further development work is required.

(*c*) *Downtakes:* The expansion of chrome-magnesite brick in downtakes due to iron-oxide absorption soon results in a destruction of the original structure. Not only do the faces of the brick tend to burst away, but whole brick may be dislodged and fall into the slag pockets. Where no silica brick are employed in the

downtakes, analyses of the slag-pocket material show it to consist of chrome-magnesite brick together with iron oxide and lime. The cinder, which can readily be removed, is still very refractory, and when ground, it makes an excellent paste for fettling back walls, etc.

(2 Acid Furnaces

Trials of chrome-magnesite brick in the back walls and ports of acid furnaces have also been made. Here again the atmosphere tends to be strongly basic because of its high iron-oxide content, and the use of chrome-magnesite brick instead of silica brick may therefore ultimately prove to be economical. Preliminary results suggest that the most serious difficulty that will be experienced is the cutting away of the basic brick by the silica sand used for fettling.

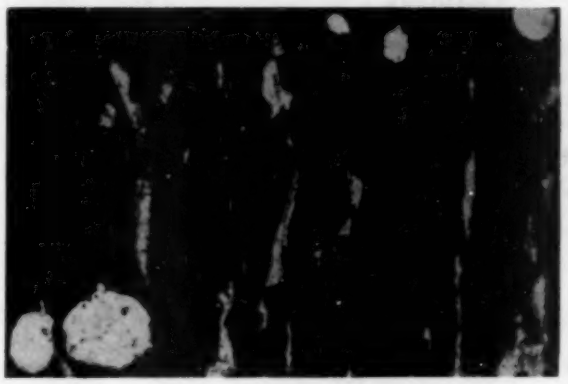

Fig. 7

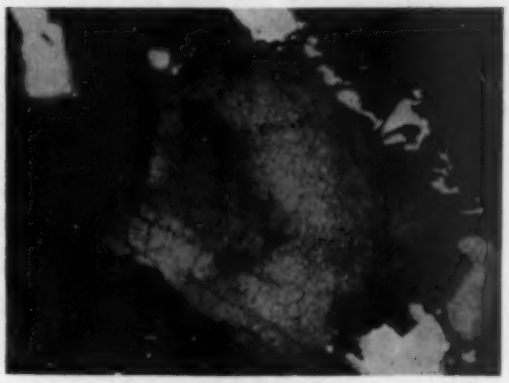

Fig. 8

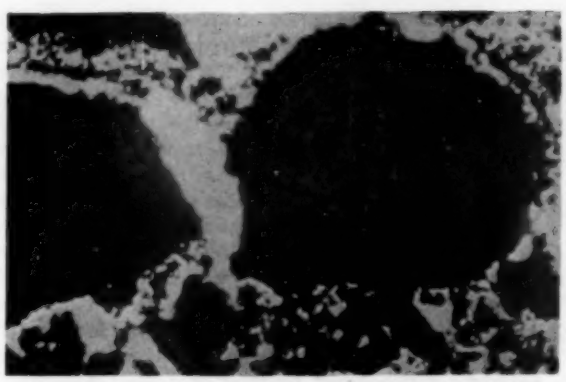

Fig. 9

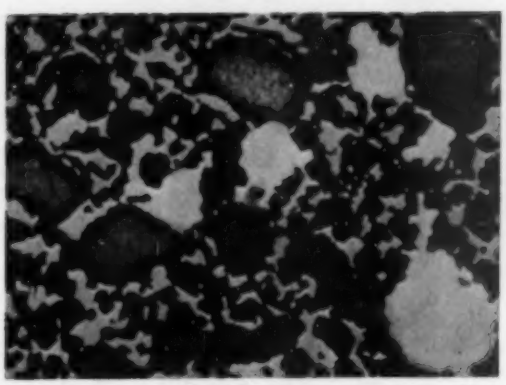

Fig. 10

FIG. 7.—Used chrome-magnesite brick; slagged surface (×40).
FIG. 8.—Used chrome-magnesite brick, 1 in. behind slagged surface (×20); note absorption of iron oxide by chromite.
FIG. 9.—Used chrome-magnesite brick, 2 in. behind slagged surface (×40); iron-oxide absorption less marked.
FIG. 10.—Slag pocket material from all-basic furnace (×40); note absorption of iron oxide by chromite.

V. Ultimate Cause of Failure of Chrome-Magnesite Brick

Figures 4, 5, and 6 illustrate the way in which chrome-magnesite brick fail when used in the construction of basic open-hearth furnaces. The working surface of the brick absorbs slag and begins to grow. So rapid is this growth that the inside of an inspection hole in the end wall of one furnace was observed to have expanded inward about $^3/_{16}$ inch after only five days' operation. In certain cases, expansions of $^1/_4$ inch on the $4^1/_2$-inch face of a brick have been observed after one week of service. Even if suitable expansion allowances were made (and these would have to be very large), the tendency of the brick surface to expand more than the back and thus to push itself into the furnace could not be overcome. Back walls and front walls have been noted in which the faces of a large number of brick had slagged together forming a monolith which protruded into the furnace (see Fig. 4), leaving a gap of several inches between this face and the remainder of the brickwork.

(1) Chemical Analyses

A comparison of the chemical analyses of a number of chrome-magnesite brick after use in open-hearth furnaces (Table III) with that of the unused brick shows that iron oxide and lime are the principal

materials absorbed. The iron-oxide content, which in the unused brick is only 12.5%, has risen to 68.3% in the sample taken from the air port of a tilting furnace. The silica content in every case is lower than that of the original brick.

(2) Microscopic Examination

Thin sections cut through used chrome-magnesite brick give a useful picture of the reactions which take place when iron oxide is absorbed. The working face has absorbed so much iron oxide that it is practically opaque (Fig. 7). It shows a peculiar orientated appearance, the crystals lying parallel to the temperature gradient. Farther in, the concentration of iron oxide falls off and the centers of chrome grains still retain the ruby-red color they show in the original brick (Fig. 8). Some of the grains are breaking up and the attack by the iron oxide is proceeding not only at the surface but along the cracks. Still farther in, there appears to be a concentration of silicates (Fig. 9), and in this region the chrome grains show little sign of iron-oxide absorption.

The refractory cinder removed from the slag pockets at the end of a campaign also shows this iron-oxide absorption in progress (Fig. 10).

(3) X-Ray Examination

Samples of used chrome-magnesite brick have been examined both by the Debye-Scherrer and the pinhole methods. The results show that the feathery surface of the used brick consists of a spinel. The pinhole photographs are essentially similar to those obtained with the chrome in the unused brick, except that the spots are somewhat blurred, suggesting that the concentration of the iron oxide dissolving in the chromite varies from the surface to the interior. This has already been demonstrated in the regions farther back (Fig. 8) by microscopic examination.

An examination of the vitrified layer which occurs several inches behind the surface shows the presence of considerable amounts of magnesia and magnesioferrite. Forsterite, which was the bond in the original brick, does not appear to be present in this region; there is silicate material, however, as yet unidentified.

VI. Conclusions

Such information as is available regarding the changes undergone by chrome-magnesite brick when used above the bath level in stationary open-hearth furnaces suggests that the main cause of deterioration is the bursting away of the brick surface caused by solid solution of iron oxide in the chromite.

A particular case of such reaction might be described by the following equation:

$$\begin{bmatrix} MgO\cdot Al_2O_3 \\ FeO\cdot Cr_2O_3 \end{bmatrix} + FeO\cdot Fe_2O_3 \rightarrow \begin{bmatrix} MgO\cdot Al_2O_3 \\ 2FeO\cdot Cr_2O_3\cdot\cdot \\ Fe_2O_3 \end{bmatrix}$$

(Solid) (Liquid) (Solid)

If the brick is free to move, the expansion of the working face (because of the absorption of 30% (approx.) of iron oxide) amounts to about 10% (linear). The brick face is in a somewhat plastic condition, and this expansion, when taking place in a side wall or roof, results in a tearing away of the surface. About six to ten weeks elapse before the amount of iron oxide absorbed is sufficient to cause this bursting on a wide scale. At this stage, the brickwork begins to "spall" badly, and new surfaces are exposed. These in turn absorb iron oxide, expand, and burst away; the process is repeated until the entire furnace lining has been destroyed by the loss of layers usually 1 to 3 in. thick.

Experiments made in the laboratory show that it is possible to make chrome-magnesite brick with the desired degree of thermal-shock resistance, yet possessing a much lower bursting expansion than those normally employed. It is hoped that, because bursting appears to be the main cause of failure of chrome-magnesite brick, it will be soon possible to obtain much longer lives, particularly in roofs and ports, and thus make possible the introduction of an all-basic furnace working at temperatures above the melting point of silica and enabling much greater outputs per square foot of hearth area to be obtained.

TABLE III

CHEMICAL ANALYSES OF SLAGGED CHROME-MAGNESITE BRICK

	Cold Metal Furnace				Hot Metal Furnace		
Origin	Back wall (%)	Air port slope (%)	Gas port slope (%)	Door jambs (%)	Port face (%)	Air port slope (%)	Original brick (%)
SiO_2	2.3	2.8	4.5	6.4	5.4	5.0	6.5
FeO (calculated as)	40.0	46.3	46.3	14.9 (Fe_2O_3)	54.6 (Fe_2O_3)	68.3 (Fe_2O_3)	12.5 (Fe_2O_3)
Al_2O_3	2.7	2.6	1.6	5.2	2.1	4.0	6.8
Cr_2O_3	21.1	17.3	11.3	29.5	21.4	6.9	30.3
MnO	2.3	2.0	1.4	0.3	1.3	0.9	
CaO	2.9	5.4	12.5	4.8	4.7	1.8	
MgO	26.3	21.0	20.7	37.6	9.7	13.7	39.8

Acknowledgment

The authors wish to thank the Oughtibridge Silica Firebrick Co., Ltd., and the United Steel Companies, Ltd., for permission to publish; Mr. Curtis, Parkgate Iron & Steel Co., Ltd., for Fig. 4; and various friends in the steel and refractories industries for information supplied.

INFLUENCE OF FLUIDITY, HYDRODYNAMIC CHARACTERISTICS, AND SOLVENT ACTION OF SLAG ON THE DESTRUCTION OF REFRACTORIES AT HIGH TEMPERATURE*

By K. Endell, R. Fehling, and R. Kley†

Abstract

Two methods for determining viscosity in the range 0.1 to 10^5 c.g.s. units (poises) at temperatures up to 1650 °C are described, and some results on slags and glasses are given. Attack on any given refractory at a given temperature increases markedly with the fluidity of the slag. Researches with hydrodynamic models show that the velocity of flow and film thickness depends more on the viscosity of the slag than on the angle of inclination of the path of flow. A new interpretation of the solvent action of slags on refractories, together with thermodynamic considerations and measurements of viscosity, permits a general mathematical treatment of the complicated changes occurring during slagging. Slag attack may be effectively lessened by choosing a refractory of low solubility and by cooling the wall to a temperature of less than 50 °C above the melting point of the slag.

I. Introduction

The hope once entertained that useful conclusions regarding the attack of slags on refractory materials could be drawn from a simple study of the melting temperature of slags or ashes has been abandoned because it is now recognized that, in practice, many factors other than the melting point of the slag influence the stability of a refractory. This is illustrated by the experience of Estep,[1] who studied the chemical composition and melting point of two thousand American coal ashes but was unable to come to any general conclusion regarding their attack on refractories or their clinkering. It has been necessary, therefore, to investigate the effect of other properties, such as fluidity, hydrodynamic characteristics, solvent power, and the mobility of dissolved substances in the slag. The results of some researches on these properties, which are described in this paper, indicate that a knowledge of all these factors will enable a correct evaluation of slag attack and will lead to an improvement in the useful life of refractories in service.

II. Fluidity of Slags at High Temperature and Slag Attack on Fireclay Refractories*

(1) Viscosity

The most significant property of the molten slag is viscosity (η) or its reciprocal, fluidity (φ), at temperatures of 50° to 200° above the melting point. For its determination, two types of apparatus, which permit measurement up to 1650°C, have been used.

(*A*) *Modified Hähnlein Viscosimeter:* The first, for use with relatively viscous slags, that is, those with a viscosity between 5 and 10^5 poises, is an adaptation of the "moving-sphere" viscosimeter of W. Hähnlein,[2] and is shown schematically in Fig. 1. A small rod with a sphere on one end is suspended from one arm of a balance so that it dips into a crucible containing the molten slag. The sphere and crucible are made of platinum or "Sinterkorund," depending upon the reactivity of the slag. A pan for weights is suspended from the other arm of the balance. The viscosity is calculated from the speed of fall of this pan when it contains a given load. The apparatus is calibrated with castor oil and with turpentine-colophonium mixtures whose viscosity has been determined at the Physikalisch-Technische Reichsanstalt. This viscosimeter can also be used as a Mohr balance to determine the density of silicate melts at high temperature.

(*B*) *Heidtkamp Viscosimeter:* The second apparatus used to measure viscosity in the range 50 to 0.1 poise is the "oscillation" viscosimeter of Heidtkamp,[3] shown in Fig. 2. A long rod, with a platinum sphere at the lower end, is attached at its upper end to an oscillating weight, which is suspended by a wire so that the sphere dips into molten slag. The suspension is then set in oscillation, and the viscosity is calculated from the damping, as measured on the scale at the upper end of the rod. The moment of rotation of the immersed part of the suspension is proportional to the rotational velocity only so long as there is no turbulence in the melt so that care must be taken to avoid turbulent flow. Because the lowest viscosity measured was not less than 0.1 poise, no difficulty arising

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* Presented at the Fortieth Annual Meeting, American Ceramic Society, New Orleans, La., March 31, 1938 (Refractories Division). Received April 27, 1938.

† Translated by J. B. Austin, Research Lab., U. S. Steel Corporation, Kearny, N. J.

[1] T. G. Estep, *Proc. Internat. Conf. Bituminous Coal, 2d Conf., Pittsburgh, Pa.*, Vol. II (1928).

* By K. Endell.

[2](*a*) *Cf.* K. Endell, Müllensiefen, and Wagenmann, *Metall u. Erz*, **29**, 368 (1932); *ibid.*, **30**, 425 (1933).

(*b*) A. Thielsch and K. Endell, "Temperature-Viscosity Relations in Liquid Glasses," *Glastech. Ber.*, **12** [3] 84–87 (1934); *Ceram. Abs.*, **14** [3] 67 (1935).

[3](*a*) G. Heidtkamp and K. Endell, "Relationship of Density and Viscosity to Temperature in the System Na_2O–SiO_2," *Glastech. Ber.*, **14** [3] 89–103 (1936); translated in *Glass Ind.*, **17** [7] 227–30 (1936); *Ceram. Abs.*, **15** [9] 272 (1936).

(*b*) K. Endell, G. Heidtkamp, and L. Hax, "Viscosity of Lime Silicates, Lime Ferrites, and Basic Open-Hearth Slags up to 1625°," *Arch. Eisenhüttenwesen*, **10** [3] 85–91 (1936); *Ceram. Abs.*, **16** [1] 46 (1937).

TABLE I

CHEMICAL COMPOSITION AND PROPERTIES OF SLAGS AND GLASSES

	Melt	Chemical Composition											Density γ	Absolute viscosity η	Kinematic viscosity η/γ	Slag attack*
		SiO_2	B_2O_3	Al_2O_3	Fe_2O_3	CaO	BaO	ZnO	PbO	MgO	Alk.	S				
14	23,983	35–40	10–15	1–5			40–45	1–5	1–5				3.19	18	5.6	0.500
15	24,401	30–35	15–20	1–5			40–45	5–10	1–5		0–1		3.10	5.0	1.6	0.145
16	24,433	35–40	5–10	1–5			40–45	5–10			0–1		3.26	24	7.4	0.074
17	23,179	40–45	5–10	1–5			40–45	5–10	1–5				3.30	32.5	9.8	0.0665
18	23,734	40–45							50–55		5–10		3.63	53	14.6	0.016
19	Schott glass (see Fig. 4) S 982	45–50	5–10	10–15		5–10	10–15	10–15					2.72	163	60.0	0.225
20	3	65–70	1–5	1–5		5–10		5–10			10–15		2.39	202	84.5	0.026
21	2	60–65	5–10	10–15		5–10					5–10		2.4**	840	350	0.0213
22	1	70–75	10–15	1–5			1–5				1–5		2.0**	2150	1075	0.0121
	Copper slag	47.34		18.8	3.02	18.63				7.57	4.57		2.6	70	25.9	0.391
	Lead slag	5.7		1.44	22.3	4.9	27.4	21.95	No data	0.4	No data	9.83	3.8**	1.2	0.32	1.69
	Iron blast-furnace slag	30.23		9.39	4.57† 3.08‡	41.26				6.86		1.74	2.5**	3.1	1.24	9.35
	Lead slag	26.3		18.5	26.8	21.4	No data	No data	No data	2.7	No data	2.1	2.9**	2.2	0.76	29.68

* Defined as decrease in length of edge of test specimen dipped in melt at 1370°C for one hour.
† FeO.
‡ MnO.
** Approximate.

from this source was experienced. The accuracy of the determination at 1650°C is ± 20%, the reproducibility ± 10%.

(2) Slag Attack

In order to correlate slag attack with slag fluidity, it was also necessary to measure the corrosive action of these slags on a refractory. Measurements of this sort have been made by Hartmann[4] and by Bartsch.[5]

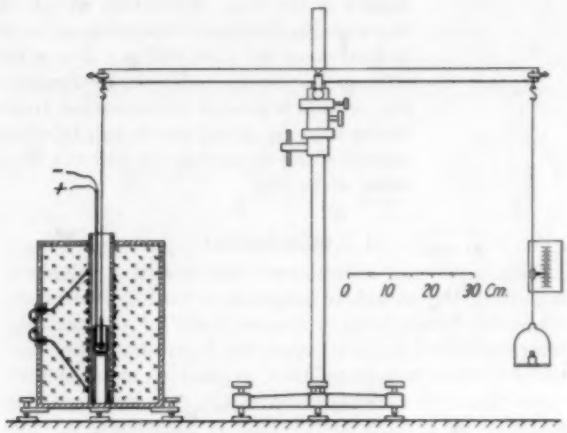

FIG. 1.—"Moving-sphere" viscosimeter used over the range 5 to 10^8 poises.

The apparatus of Bartsch, developed at the Schott and Genossen Glass Works (see Fig. 3) was adopted for this work. Four test pieces of square cross-section, 10 mm. on a side and 110 mm. long and made of a standard fire clay, were dipped into molten slag, contained in crucible T_1. The measurements were made at 1370°C. When the furnace had come to equilibrium, the fireclay holder, H, in which the test pieces were set, was lowered until the pieces were immersed to a depth of 70 mm. The decrease in cross-section during the exposure was used as a measure of attack, the results being reported as decrease in length of edge for a position 20 to 40 mm. under the liquid surface after a 1-hour exposure.

The composition of the standard test pieces (fire clay V107) was as follows: Al_2O_3 34.88, SiO_2 63.90, Fe_2O_3 0.65, CaO 0.15, and $K_2O + Na_2O$ 0.27%. Other properties were porosity 4%, bulk density 2.3, firing temperature Seger cone 33, and mean pore size0. 1μ. The composition, density, viscosity, and corrosive power of the several slags tested are given in Table I.

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[4] F. Hartmann, "Viscosity of Slags and Its Application to Slagging of Refractory Brick," *Ber. deut. keram. Ges.*, **15** [7] 375–90 (1934); *Ceram. Abs.*, **14** [5] 119 (1935).

[5] (*a*) O. Bartsch, "Glass Attack on Refractory Materials and Their Testing," *Ber. deut. keram. Ges.*, **15** [6] 281–317 (1934); *Ceram. Abs.*, **13** [2] 34 (1934).

(*b*) O. Bartsch, "Determination of Slag Attack with the Crucible Method," *Ber. deut. keram. Ges.*, **19**, 413–26 (1938).

The variation of slag attack with fluidity (reciprocal of viscosity), as reported by Endell and Wens[6] for the slags described in Table I, is presented graphically in Fig. 4, which shows clearly that the attack increases

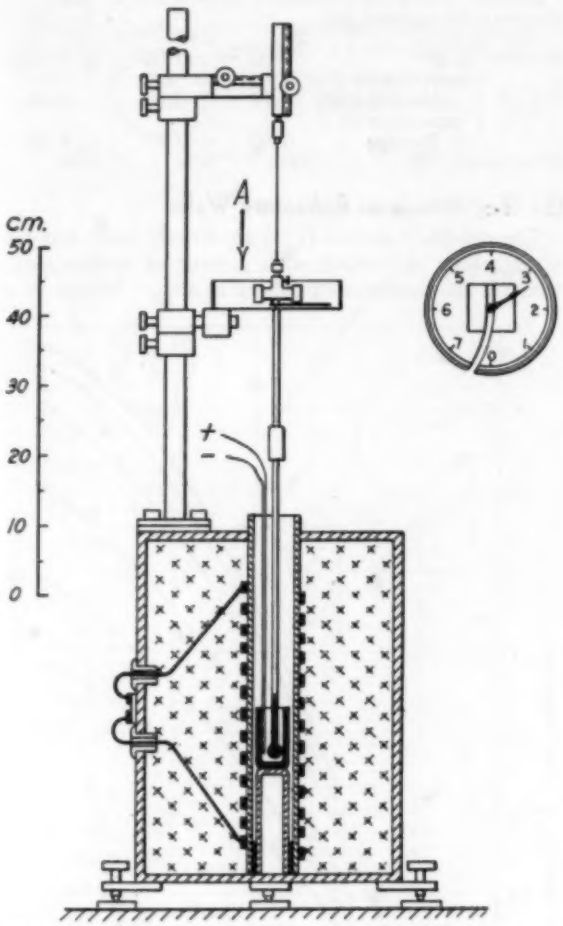

FIG. 2.—"Oscillation" viscosimeter used over the range 50 to 0.1 poise.

rapidly with fluidity but is almost independent of chemical composition. This variation with fluidity, or viscosity, is given by the expression,

$$A = 10/\eta = 10\varphi. \qquad (1)$$

Where A = attack expressed as loss in edge-length (mm./hr.)

(3) Density of Slag

Another factor influencing the transport of the dissolved material and hence the severity of attack is the density of the molten glass or slag. And just as in the case of fluidity, the density changes with increasing temperature in such a way as to cause increased attack.

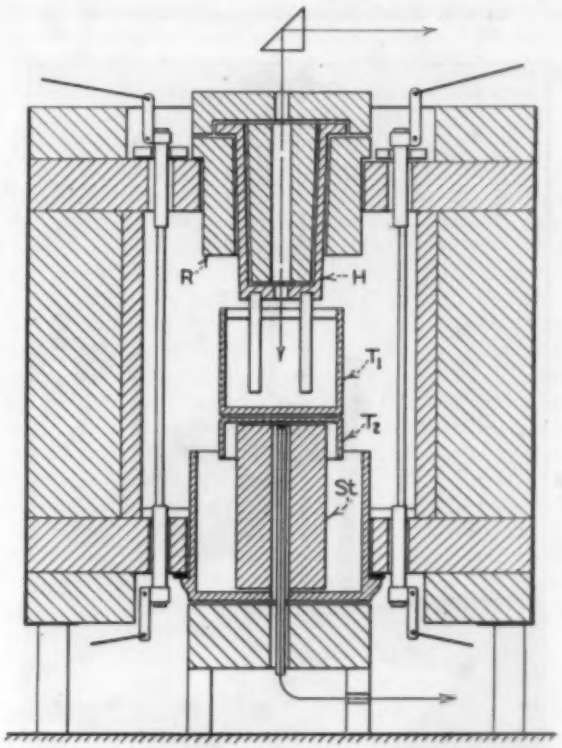

FIG. 3.—Cross-section of apparatus used to measure slag attack.

Little mobility is observed in slags with a viscosity above 500 poises, and in most slags drops of liquid form when the viscosity falls below 50 poises.[7] It is in

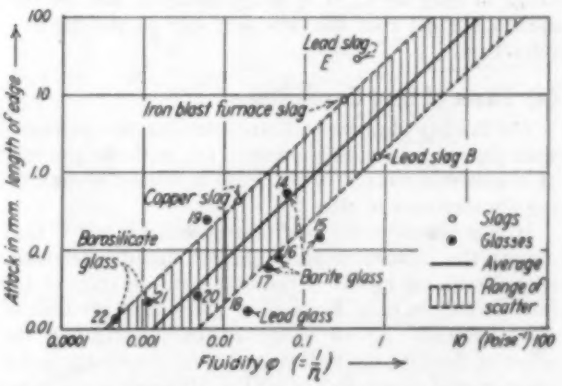

FIG. 4.—Increase of slag attack with increasing fluidity.

[6] K. Endell and C. Wens, "Relation between Attack on Fire Clay and the Density and Fluidity of Glasses and Slags at High Temperatures," *Glastech. Ber.*, **13** [3] 78–86 (1935); *Ceram. Abs.*, **15** [1] 15 (1936); see also *Ind. Heating*, **4**, 143 (1937).

[7] (*a*) K. Endell and C. Wens, "Temperature-Viscosity Relationships of Coal Slags: I, Methods of Investigation and Results"; (*b*) P. Rosin and R. Fehling, "II, Conclusions for Firing Techniques," *Z. Ver. deut. Chem.* (*Beiheft*), No. 12; abstracted in *Angew. Chem.*, **48**, 76–77 (1935); *Ceram. Abs.*, **17** [5] 202 (1938).

the intermediate range, therefore, that slagging action is most severe, and according to equation (1), the attack is between 0.01 and 0.2 mm. per hr. Remembering that many slags pass from their melting point to a state in which liquid drops are formed within a

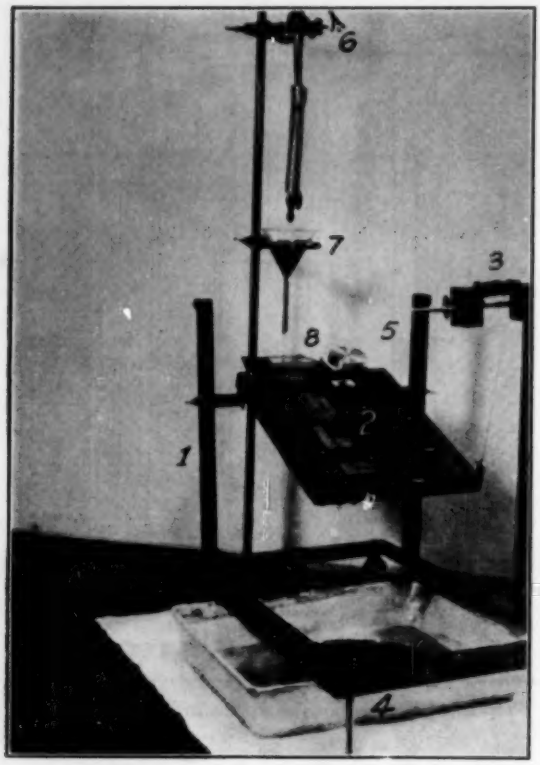

FIG. 5.—Model used to investigate the influence of variables on fluid flow.

range of only 50°C, it is not difficult to see the tremendous effect that slag viscosity has on the life of a refractory.

(4) Effect of Slag Composition

The fluidity of molten silicate solutions also decreases with the amount of SiO_4 present, *i.e.*, with the amount of tetrahedral silicon, in the sense it is used in describing the structure of glass.[8]

It was observed by Heidtkamp and Endell[3(a)] that among the molten alkali disilicates fluidity decreases with increasing radius of the alkali ion, in spite of the fact that there is an increase in the weight per cent of silica present. At all temperatures investigated, the order of fluidity, ion radius, and silica content was the same as that shown in Table II. Although a quantitative generalization is not possible on the basis of these data alone, they are sufficient to show the order of magnitude and the qualitative effects to be expected.

[8] B. E. Warren and A. D. Loring, "X-Ray Diffraction Study of the Structure of Soda-Silica Glass," *Jour. Amer. Ceram. Soc.*, **18** [9] 269–76 (1935).

TABLE II

RELATION BETWEEN VISCOSITY, FLUIDITY (AT 1400°C), SILICA CONTENT (IN WEIGHT PER CENT), AND ALKALI-ION RADIUS (IN DISILICATE MELTS)

Property		Li	Na	K
Temp. above melting point		380°	524°	424°
Viscosity (η) (poises) at 1400°C		20	<40	<70
Fluidity ($1/\eta$)		0.05	> 0.025	> 0.0143
Ion radius (A°)	according to Goldschmidt	0.78	< 0.98	< 1.33
	according to Pauling	0.60	< 0.95	< 1.33
SiO_2 (weight %)		80	>67	>56

(5) Slag Attack on Refractory Walls

The results of section II (4) are strictly valid only for a refractory in contact with a bath of molten slag, which is the condition obtaining in a steel furnace or a

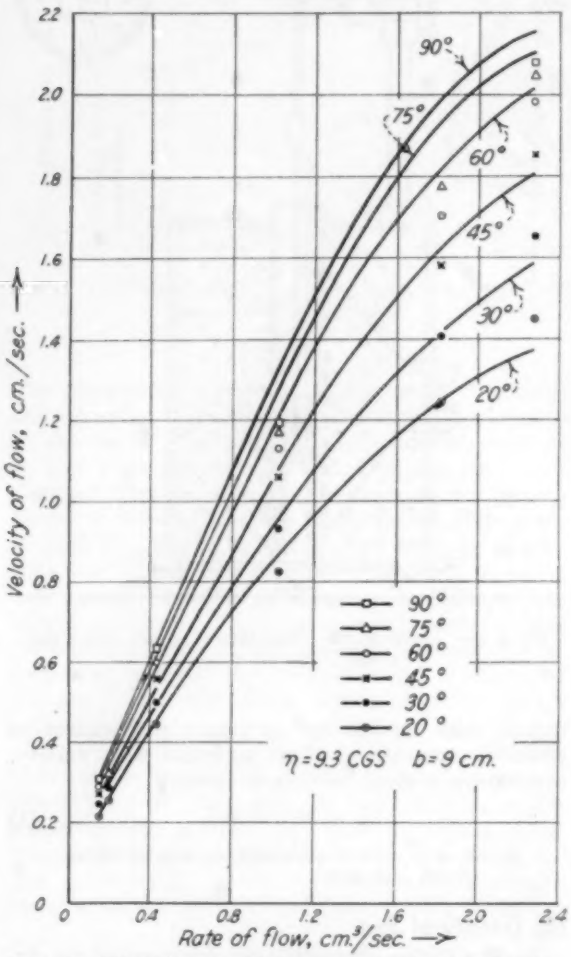

FIG. 6.—Variation of velocity of flow of oil with rate of flow for different angles of inclination.

glass tank. There are many other applications, such as in steam boilers in which there is no bath of slag but merely a thin film running over the refractory surface. The thickness of this film, which has a great influence on diffusion in the film, is controlled by two

factors, *viz.*, (*a*) the feed, or supply, of slag, *i.e.*, the quantity of flying slag deposited on the refractory per hour, and (*b*) the removal of the slag or the speed at which it drains along the refractory.

III. Experiments with Models Using Oil*

To investigate these factors more thoroughly, a series of experiments was made with a hydrodynamic model. These studies were intentionally made at room temperature to permit the exact determination of experimental conditions. The studies in themselves yield some useful conclusions about behavior at high temperatures, provided the geometric and hydrodynamic conditions are similar at each temperature, which is true when the ratio of the forces of inertia to the frictional forces within the flowing material is constant. This relation is given by the Reynolds number,

$$R = \frac{\text{velocity} \times \text{length of path of flow}}{\text{kinematic viscosity}}.$$

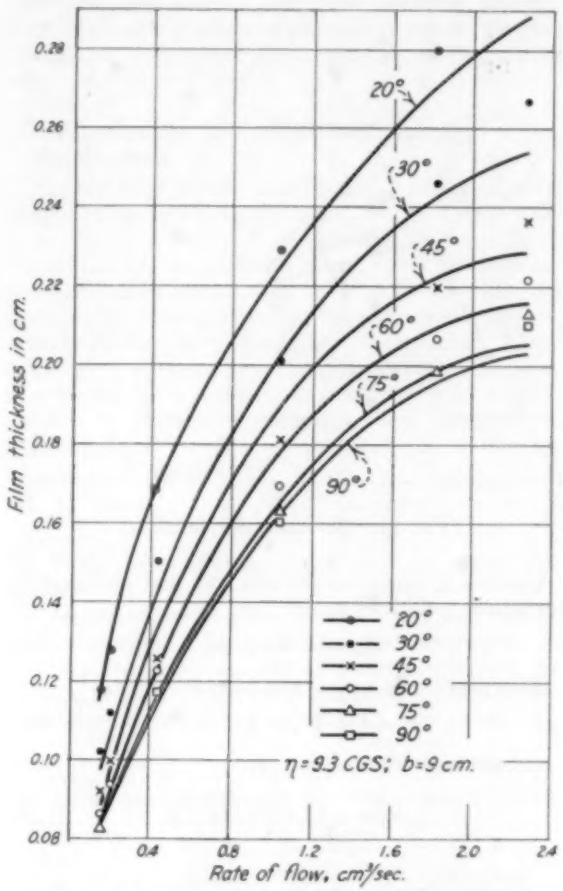

FIG. 7.—Variation of film thickness with rate of flow for different angles of inclination.

Experiments with the channel viscosimeter, used in the ceramic industry,[9] show that it can not be used to determine velocity of flow because it holds only a few cubic centimeters of liquid. With such a short path of flow, the kinetic energy of the liquid is so small that the time of flow becomes practically infinite. To avoid this difficulty, an apparatus was built which keeps the liquid in constant flow.

(1) Apparatus and Procedure

The apparatus (Fig. 5) consists of a support (1), a flow channel in which the liquid flows (2), and a device for changing the inclination of the channel to the horizontal (3). The support is equipped with set screws (4) which allow it to be properly levelled. The channel in which the liquid flows is a glass plate fixed between two angle irons in such a way that the width can be varied from 0 to 9 cm. Under the plate is a scale with millimeter divisions, which is used to measure length along the channel. Film thickness is measured with a micrometer screw (5) supported over the channel as shown. With this screw, the thickness can be determined to 0.05 mm. The test liquid flows from a reservoir (6) to a glass funnel (7), held at constant height, whence it flows into another reservoir (8) attached to the upper end of the channel. From this reservoir, it flows over a sharp edge on to the glass plate, whose angle of inclination can be varied between 0 and 90°.

Two oils, whose viscosity was 9.3 and 4.5 poises, respectively, were used to determine the influence of viscosity. The feeding of liquid varied with the width of the channel between 0.15 and 2.3 sq. cm. per sec.

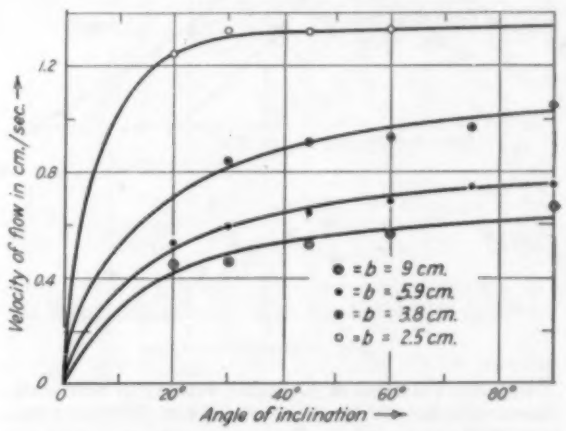

FIG. 8.—Variation of velocity of flow with angle of inclination for different widths of path.

After the rate of oil supply to the channel had been adjusted, alumina dust was scattered on the middle of the flowing film to serve as a speed indicator, and the velocity of flow was measured by determining the time required for a given particle to move 20 cm. At the same time, film thickness was measured with the

* Experiments with models using oil to study (1) the hydrodynamic relations between velocity of flow and film thickness and (2) the viscosity, slag supply, and angle of inclination of the path of flow by R. Kley.

[9] See footnotes 6 and 7.

micrometer screw. The results of these measurements are shown in Figs. 6, 7, and 8.

It is interesting to see how these experimental data compare with the equation deduced by Fehling[10] from general hydrodynamic principles.

Symbols Used

W_0 = velocity of flow (cm./sec.).
W_m = mean velocity of flow (cm./sec.).
d = film thickness (cm.).
η = viscosity (poises).
ν = kinematic viscosity (cm.²/sec. ($= \eta/\gamma$)).
α = angle of path of flow to horizontal.
γ = density (g./cm.³).
g = acceleration of gravity (cm./sec.²).
V = quantity of flow (cm.³/sec.).
b = width of path of flow (cm.).

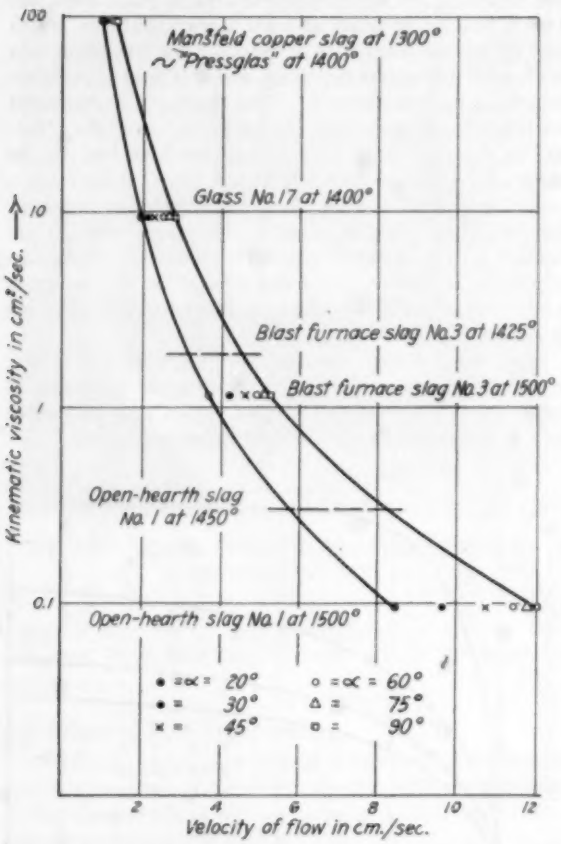

FIG. 9.—Variation of calculated velocity of flow with kinematic viscosity for different slags at different temperatures.

For each square centimeter of film surface, there is a tangential force, T, necessary to produce the rate of flow, W, which is given by

$$T = \eta \frac{dW}{dx} \text{ g/cm.}^2 \tag{2}$$

[10] R. Fehling, "Attack of Coal Slags on Refractory Brick," *Feuerungstechnik*, **26**, 33–35 (1938); *Ceram. Abs.*, **17** [8] 280 (1938).

With the boundary conditions,

$$x = 0,\ W = 0.$$
$$x = d,\ W = W_0.$$

Then $dW/dx = W_0/d$.

$$W_0 = T \cdot d/\eta. \tag{2a}$$

On the other hand, the tangential force, T, can be expressed in terms of gravity as

$$T = d \cdot \gamma g \cdot \sin \alpha. \tag{3}$$

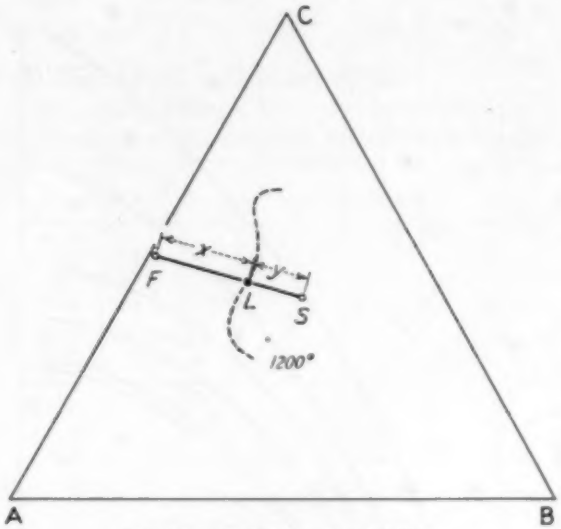

FIG. 10.—Definition of solubility.

Combining equations (3) and (2*a*) and changing to equivalent quantities we get

$$W_0 = d^2 \cdot \sin \alpha \cdot g/\nu. \tag{4}$$

The quantity factor, V, can be expressed as

$$V = b \cdot d \cdot W_m = b \cdot d \cdot W_0/2. \tag{5}$$

Combining with equation (4),

$$W_0 = \sqrt[3]{\frac{4 \cdot g \cdot \sin \alpha}{\nu} \left(\frac{V}{b}\right)^2}, \tag{6}$$

and

$$d = \sqrt[3]{\frac{2 \cdot \nu}{g \cdot \sin \alpha} \left(\frac{V}{b}\right)}. \tag{7}$$

Equations of essentially the same form have been found to represent the data in Figs. 6, 7, and 8.

$$\text{Then } W_0 = 0.85 \cdot Re^{0.05} \sqrt[3]{\frac{4 \cdot g \cdot \sin \alpha}{\nu} \left(\frac{V}{b}\right)^2} \tag{6a}$$

and

$$d = 1.31 \cdot Re^{0.02} \sqrt[3]{\frac{2 \cdot \nu}{g \cdot \sin \alpha} \left(\frac{V}{b}\right)}. \tag{7a}$$

Where Re = Reynolds number, $\frac{W_0 \cdot d}{\nu}$.

Comparison of equations (6) and (6*a*) and (7) and (7*a*) shows that the agreement is gratifying. The chief difference is in the appearance of the Reynolds

number in the equations for the experimental observations, and this difference is relatively insignificant. Careful measurements in the region of high velocity revealed no significant variation from these relations until the flow became turbulent.

The constants, 0.85 and 1.31, in equations (6*a*) and (7*a*), respectively, take care of certain factors which were neglected in the derivation of equations (6) and (7), *viz.*, that the velocity of flow is greater in the center of the film than at the channel wall and that the film is thicker at the channel wall than in the middle. Although these factors have some academic interest, they have little practical significance because they are essentially constants of the apparatus and vary with experimental conditions.

(2) Conclusions Regarding Metallurgical Applications

The foregoing results show that slag attack depends largely on the rate of supply of slag and on the viscosity of the slag and only to a small extent on the angle of inclination of the refractory wall. To demonstrate the relative importance of these factors, a few examples are calculated using slags and glasses whose composition and density have already been determined. These calculations of necessity are only approximate because, in applying the equations, it is necessary to make a number of arbitrary simplifications and assumptions. For example, Reynolds number is neglected, so that the relation used becomes,

$$W_0 = \left(\frac{4 \cdot g}{b^2}\right)^{1/3} \left(\frac{V^2 \cdot \sin \alpha}{\nu}\right)^{1/3} \qquad (8)$$

It is further assumed that ν is 20 cu. cm. per sec. and that b is 1 m.

Calculations were made for five slags and glasses with results shown in Table IV. The composition of two of these materials, Schott glass No. 17 and the Mansfeld copper slag, is given in Table I. Data for the remainder are given in Table III. The results are

TABLE III

CHEMICAL COMPOSITION OF AN OPEN-HEARTH SLAG, BLAST-FURNACE SLAG, AND "PRESSGLAS"

	Open-hearth furnace slag (%)	Granulated blast-furnace slag (%)	"Pressglas" (%)
SiO_2	9.6	31.8	74.8
Al_2O_3	1.5	15.7	1.2
TiO_2	0.3		
FeO	9.8	1.8	
Fe_2O_3	6.8		0.04
MnO	8.6	0.8	
CaO	49.9	41.0	8.1
MgO	6.5	4.6	0.4
P_2O_5	3.2	SO_3 0.3	BaO 0.1
Total S	0.2	0.7	K_2O 0.5
		Ignition Loss 2.2	Na_2O 14.8
Total	96.4	98.9	99.94

also shown graphically in Fig. 9. Points for the "Pressglas" are not shown because they are very close to those for the Mansfeld slag. The data for the open-hearth slag show clearly the great influence of the change in viscosity with temperature and the small influence of angle of inclination, because the velocity of flow at an angle of 90° and a temperature of 1450°C is less than that at an angle of 20° and a temperature of 1500°C; *i.e.*, even though the angle of flow has been increased from 20° to vertical (90°), the slag is so much more viscous at 1450°C than at 1500°C that the net rate of flow is less.

This means that the design of the furnace, insofar as the slope of the walls is concerned, has practically no influence on the resistance of the refractory to attack by slag. A real improvement may be effected, however, by cooling the wall to increase the viscosity of the slag in contact with the refractory so that a protective layer of slag is built up.

IV. Solubility, Erosion, and Slag Attack at High Temperature*

(1) Solubility (Definition and Determination)

By solubility is meant that quantity of solid refractory material which the slag can dissolve without partially or completely freezing, *i.e.*, it is the amount required to saturate the slag. It makes no difference

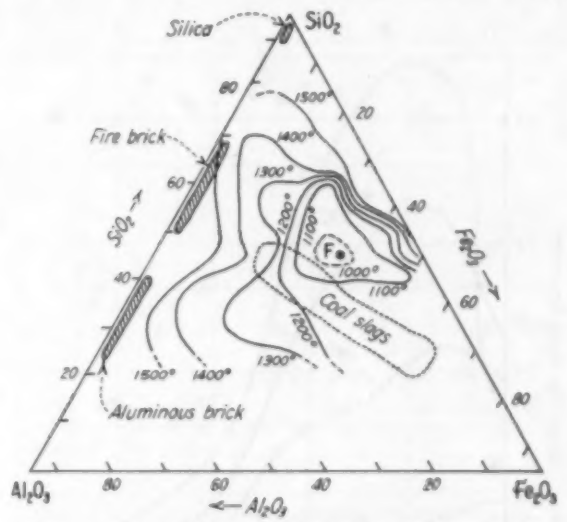

FIG. 11.—A.S.T.M. softening-point isotherms in the system Al_2O_3–Fe_2O_3–SiO_2 (after Moody and Langan).

whether this solvent action occurs by simple solution of the solid material in the form in which it exists on the wall or whether there is a change in chemical composition by reaction between slag and refractory.

Solubility, which is expressed in per cent by weight of the solvent slag, is the most fundamental factor controlling slag attack, and it is determined as follows: When composition is expressed on the triangular three-component diagram of Gibbs, the composition of all mixtures between two substances which occur within the ternary system (*e.g.*, points *F* and *S* in Fig. 10) lies on a straight line joining the two points representing these substances. This line does not necessarily

* By E. R. Fehling.

indicate the manner in which solution, L, is formed, but this does not matter so long as equilibrium is attained and the system is completely liquid. This straight line is cut by the melting-point isotherms in the system (in Fig. 10, the 1200° isotherm is shown), from which it is possible to read off the melting point corresponding to different mixtures. The relative proportions of the two substances present at the melting point are determined by applying the lever rule to the portions of the line on either side of the intersection; for example, in Fig. 10, $x/(x + y)\%$ of S is in equilibrium with $y/(x + y)\%$ of F at 1200°.

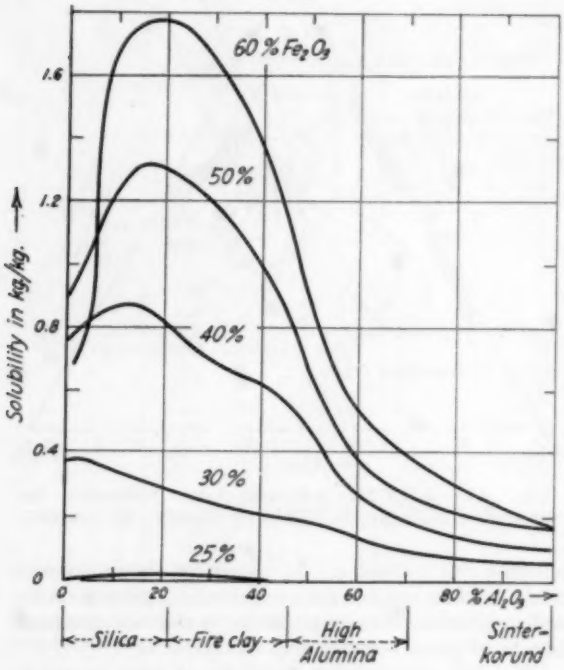

FIG. 12.—Influence of iron oxide on solubility of refractories at 1200°C (taken from Fig. 11).

The application of such a diagram is obvious. If F represents the composition of the refractory and S that of the slag, then L is the solubility of F in S at 1200°. That is, the solubility is $y/x \cdot 100$ in weight per cent based on pure slag. In this paper, solubility is expressed in kilograms of dissolved material per kilogram of slag. It is to be emphasized that the solubility thus defined is the true solubility, *i.e.*, the amount dissolved after sufficient time to allow equilibrium to be reached, and it is the maximum amount of refractory the slag will dissolve at the given temperature.

TABLE IV

DENSITY, VISCOSITY, AND CALCULATED VELOCITY OF FLOW OF SLAGS AND GLASSES AT 1300° TO 1500°C (CM./SEC.)

Material	Temperature (°C)	Density γ	Viscosity C.g.s. η	Viscosity Cm.²/sec. $\nu = \eta/\gamma$	Calculated velocity of flow (cm./sec.) for different angles of inclination 20°	30°	45°	60°	75°	90°
Open-hearth slag	1500	3.3	0.3	0.091	8.38	9.52	10.69	11.4	11.9	12.0
Blast-furnace slag	1500	2.6	3	1.15	3.60	4.09	4.59	4.91	5.09	5.13
Schott glass No. 17	1400	3.3	30	9.1	1.81	2.05	2.30	2.46	2.56	2.58
Copper slag	1300	2.6	240	92	0.83	0.95	1.06	1.14	1.18	1.19
'Pressglas"	1400	2.2	240	109	0.79	0.90	1.0	1.08	1.12	1.13

In order to apply this method, three conditions must be met, *viz.*, (*a*) the chemical composition of refractory and slag must be known; (*b*) the composition of the refractory and slag must lie within a ternary system; and (*c*) the most important melting-point isotherms must be known. The last two conditions severely limit the usefulness of the method because only a few systems have been investigated, but it is possible to treat fireclay, silica, and alumina refractories and a great many coal slags in an approximate though satisfactory way by assuming them to be included in the system $Al_2O_3 + SiO_2 + Fe_2O_3 = 95\%$, where the other 5% represents a constant content of CaO + MgO. The A.S.T.M. softening isotherms in this system have been studied by Moody and Langan[11] with results shown in Fig. 11.

The influence of additions of iron oxide on the solubility at 1200°C of the refractories mentioned is shown in Fig. 12. At this temperature, slag attack begins at a composition containing about 25% Fe_2O_3 and increases rapidly with increasing iron content in the slag. It is much greater for normal fireclay refractories than for the more costly high alumina refractories. Up to 50% Fe_2O_3 in the slag, the solubility of silica brick increases; above 50% Fe_2O_3, the solubility decreases. In no case is the solubility directly proportional to the content of iron oxide.

The variation of solubility with temperature is shown in Fig. 13. The corroding slag in this case consists of the eutectic in the system Al_2O_3–SiO_2–Fe_2O_3 (Fig. 11). The solubility at 1200° falls steadily with increasing alumina content, but at 1300° two sharp maxima appear at 25% and 80% Al_2O_3. At a still higher temperature, these peaks become sharper, and the position of the alumina-rich maximum is displaced toward the composition of mullite and sillimanite (about 65% Al_2O_3). At high temperatures, the aluminous refractories are most resistant to the particular slag considered (*viz.*, F in Fig. 11) when they contain about 50% Al_2O_3, which is about the composition of kaolinite and other natural deposits.

[11] A. H. Moody and D. D. Langan, "Fusion Temperature of Coal Ash as Related to Composition," *Combustion*, **6** [8] 13–20 (1935); *Ceram. Abs.*, **15** [1] 43 (1936).

(2) Reaction Equations for Slag Attack

Using the principles which have been described in preceding sections and the principles of dimensional analysis, Fehling[10] has developed a reaction equation, which, for a given furnace and a given firing practice, takes the following form:

$$a = C \cdot L_0 \frac{T^{3/5}}{\eta^{3/5}} (\theta BA)^{1/5}. \qquad (9)$$

Where a = slag attack perpendicular to wall surface (cm./sec.).
L_0 = solubility (kg. refractory/kg. slag).
T = absolute temperature of refractory surface.
η = viscosity of slag (poises).
θ = fraction of total ash which flies to wall.
B = heat liberated in firing chamber (K cal./m.^{3}/hr.).
A = ash content of coal (g./g.).
C = constant depending on furnace.

This equation contains so many variables and is based on such a long chain of assumptions and experimental results that only a direct and exact determination of slag attack under well-defined conditions can be used to test its correctness. Fortunately, this is now possible through the recently published work of Fettke and Stewart.[12] These investigations were made with a powdered coal flame, so controlled that 500 lb. of ash were blown into the firing chamber, the walls of which were made of different kinds of refractory brick but always contained a standard fireclay brick for comparison. It is the attack on this brick which provides a test for equation (9). The composition of the brick was SiO_2 51.9, Al_2O_3 42.5, Fe_2O_3 1.5, TiO_2 2.5, CaO 0.4, MgO 0.2, and porosity 18%. Fifteen experiments of 100 hours' duration were made. The fuel was powdered coal of different ash content and of different ash composition. Although this circumstance complicates things somewhat, because the system is not ternary but contains four or five substances which change their proportions in the slag, nevertheless, some interesting results were obtained.

The conditions under which the calculation was made are as follows:

(1) The solubility of this fireclay refractory in slags Nos. 1 to 15 at the temperature in question was calculated by the graphical method already described.

(2) The viscosity for 20% Fe_2O_3 was taken from Fig. 14, which is based on measurements by Endell and Wens.[7(a)]

(3) In each calculation, the temperature above the melting point was used rather than the absolute temperature. This was necessary because the melting points reported by Fettke and Stewart do not agree with those of Moody and Langan on account of a difference in the amount of CaO and MgO present. The large temperature coefficient near the melting point makes a comparison useless unless some such reduction to a common zero can be made.

(4) It is assumed that the viscosity at the melting point is 1000 poises, an assumption based on the data of Endell and Wens. Because of the rapid increase in viscosity with decreasing temperature in the region above 1000 poises, the result is not sensitive to the value of η.

(5) The observed erosion was reduced to constant slag supply by means of the quantity $(\theta BA)^{1/5}$.

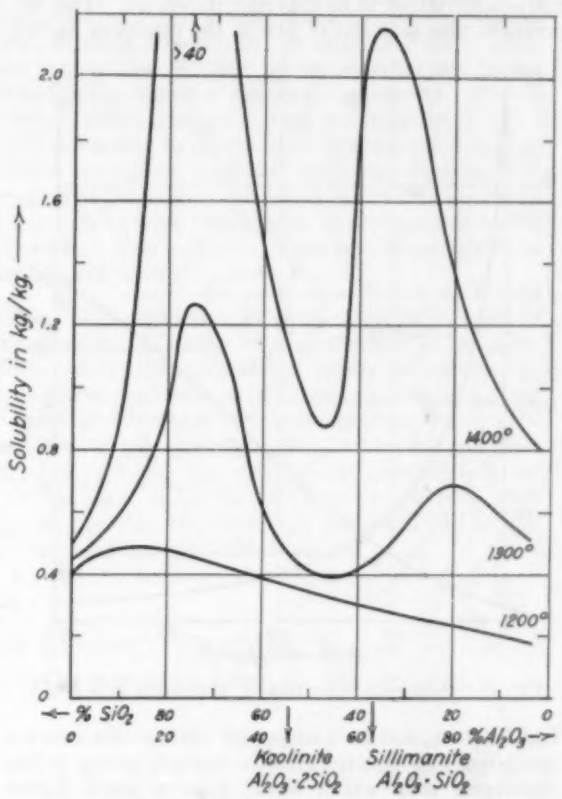

FIG. 13.—Solubility of different refractories at different temperatures in a slag having the eutectic composition, F (Fig. 11).

(6) The change in the temperature function ($T^{3/5}$) is insignificant because it changes but 6% in going from 1300° to 1500°C.

On the basis of these considerations, the reduced values of slag attack are compared in Fig. 15 with the predictions of equation (9). The calculated values of slag attack, of course, are only relative because the absolute value of some of the constants in equation (9) can not be determined.

The agreement shown in Fig. 15 is most satisfactory, especially when the following sources of error are considered:

(1) In spite of care taken to insure uniformity, there is probably some variation in the fireclay brick.

(2) The melting point, viscosity, and erosion were determined in three different materials, *viz.*, (*a*) Moody and Langan (synthetic ashes with constant content of (CaO + MgO)), (*b*) Endell and Wens (synthetic slags

[12] C. R. Fettke and W. E. Stewart, "Slagging Action of Western Pennsylvania Coals on Different Types of Refractories in a Small Pulverized Coal Installation," *Carnegie Inst. Tech., Coöp. Bull., Mining & Met. Invest.*, No. 73, 90 pp. (1936); *Ceram. Abs.*, **17** [1] 24 (1938).

and German coal ashes), and (*c*) Fettke and Stewart (American coal ashes).

(3) The calculation of the diffusion coefficient from viscosity, which is based on the kinetic theory of heat and is inherent in equation (9), has not yet been established beyond question for slags.

The results of the comparison shown in Fig. 15, however, are so satisfactory that they give strong support to the method of calculation employed. The only marked deviation is in experiment No. 12. This experiment also falls out of line in the results of Fettke

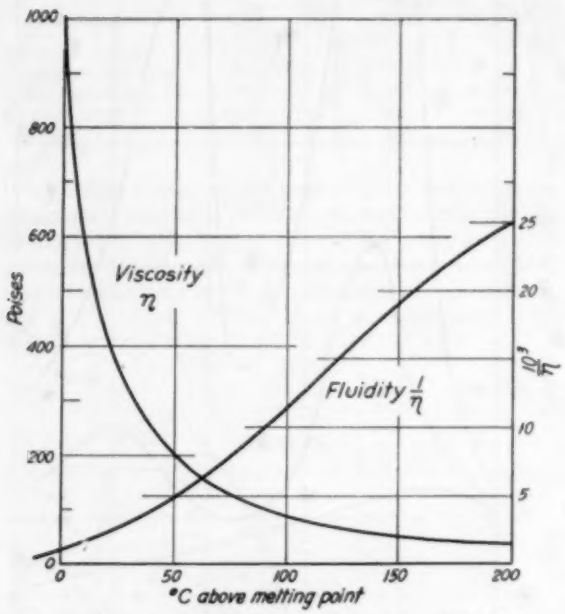

FIG. 14.—Viscosity of a coal slag containing 20% Fe_2O_3.

and Stewart, and it is suspected that in this case the powdered coal was imperfectly burned, giving a slag containing coke which would have a much higher viscosity.[6]

It should be noted that the straight line representing the average in Fig. 15 does not go through the origin. The reason for this can be seen from Fig. 16. The observed erosion has been corrected here for that part of the solubility which depends on temperature and on slag composition to leave the effect of viscosity alone. The result is as follows:

$$\frac{a}{L_0} = \frac{\text{constant}}{\eta^{0.6}} = f(T). \qquad (10)$$

Figure 16, therefore, shows the influence of the temperature variation of viscosity under approximately equal conditions. For a temperature of more than 50°C above the melting point, calculated and measured values are in agreement. For a temperature of less than 50°C above the melting point, the measured erosion is practically zero, because the surface tension of the slag prevents wetting of the wall with consequent lessening of attack on the refractory. This state is first attained at a viscosity of about 200 poises, and because the reaction equation applies only to this homogeneous film, the deviation is explained.

The results as given apply strictly only to attack of coal ash on the fireclay brick which served as a standard. Fettke and Stewart studied a great many other refractories, and when the composition of one of these lies within the system Al_2O_3–SiO_2–Fe_2O_3, a similar correlation can be made.

V. Conclusions

(1) Slag attack may be considered as a simple solution process even when a chemical change is involved. One of the most important factors governing such attack is the diffusion coefficient of the dissolved material in the slag. The extraordinarily rapid increase of slag attack with increasing temperature is the result of the combined influence of increased solubility, fluidity, and diffusivity.

(*a*) The influence of higher solubility arises not so much from the increase in the concentration at saturation as in the increase in concentration gradient with

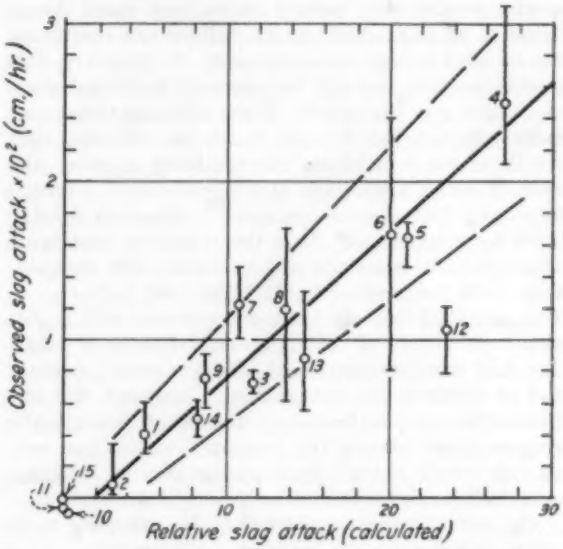

FIG. 15.—Correlation between calculated relative attack and observed attack.

its consequent accelerating effect on diffusion. In spite of the thinness of the film, only rarely does it approach saturation; *e.g.*, Fettke and Stewart found that the slag was only 15 to 25% saturated.

(*b*) With increasing fluidity, the velocity of flow of the film and the film thickness is lowered, which results in a more rapid feeding of fresh and unsaturated slag. Velocity of flow and film thickness can be calculated from equations (6*a*) and (7*a*). For average conditions of firing and for the slags whose viscosity is represented by the line in Fig. 14, the following summary is given:

Temperature above melting point (°C)	0	50	100	150	200
Viscosity (poises)	1000	200	90	50	40
Velocity of flow (mm./hr.)	52	89	116	142	153
Film thickness (mm.)	7.0	4.1	3.1	2.6	2.4

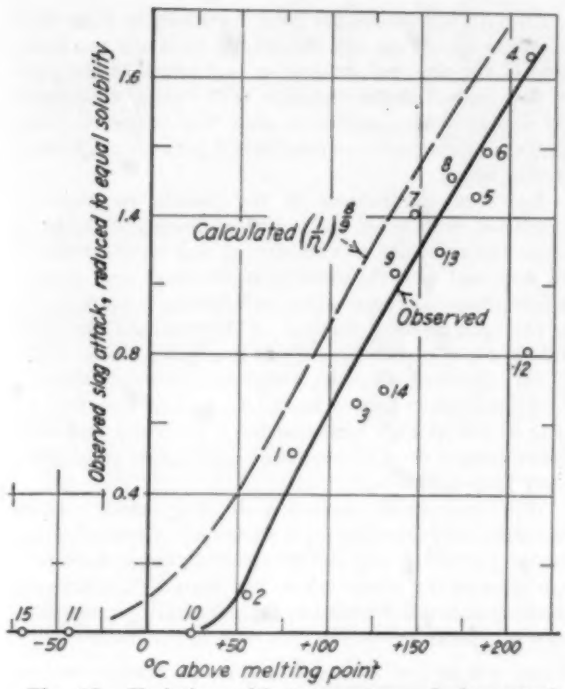

Fig. 16.—Variation with temperature of slag attack corrected to equal solubility.

On a thin wall, that part of the film next the wall may become so plastic that it acts as an insulator. Such an unreactive plastic film is the best conceivable protection of the refractory against slag attack.

(*c*) The influence of increased diffusivity needs no detailed explanation because the chemical exchange necessary for reaction depends entirely on molecular transport in the slag.

In considering viscosity, it is necessary to differentiate between a change in viscosity due to change in temperature and one due to a change in chemical composition. The foregoing discussion has pointed out specifically that the decrease in viscosity with increasing Fe_2O_3 content is not accompanied by a corresponding change in slag attack. In this case, the rate of diffusion is influenced not only by viscosity but also by the changing ion radius of the slag components. This is a subject which deserves further investigation.

(2) According to the reaction equation (9), the combustion variables, such as load, ash content, and amount of flying slag, exert only a small influence on slag attack because they appear in the equation as the $^1/_9$ power. This surprising result may be explained on the following basis:

Appreciable resistance to slagging is attained only in two ways, *viz.*, (1) selection of a refractory of low solubility and (2) reduction of the surface temperature of the refractory to less than 50°C above the melting point of the slag. The data show that under ordinary conditions the slag is less than 25% saturated and that chemical exchange and reaction can proceed only by diffusion; there is always an excess of relatively pure slag in the film, therefore, and an additional supply of virgin slag has but little effect.

A graphical summary of all these factors is given in Fig. 17.

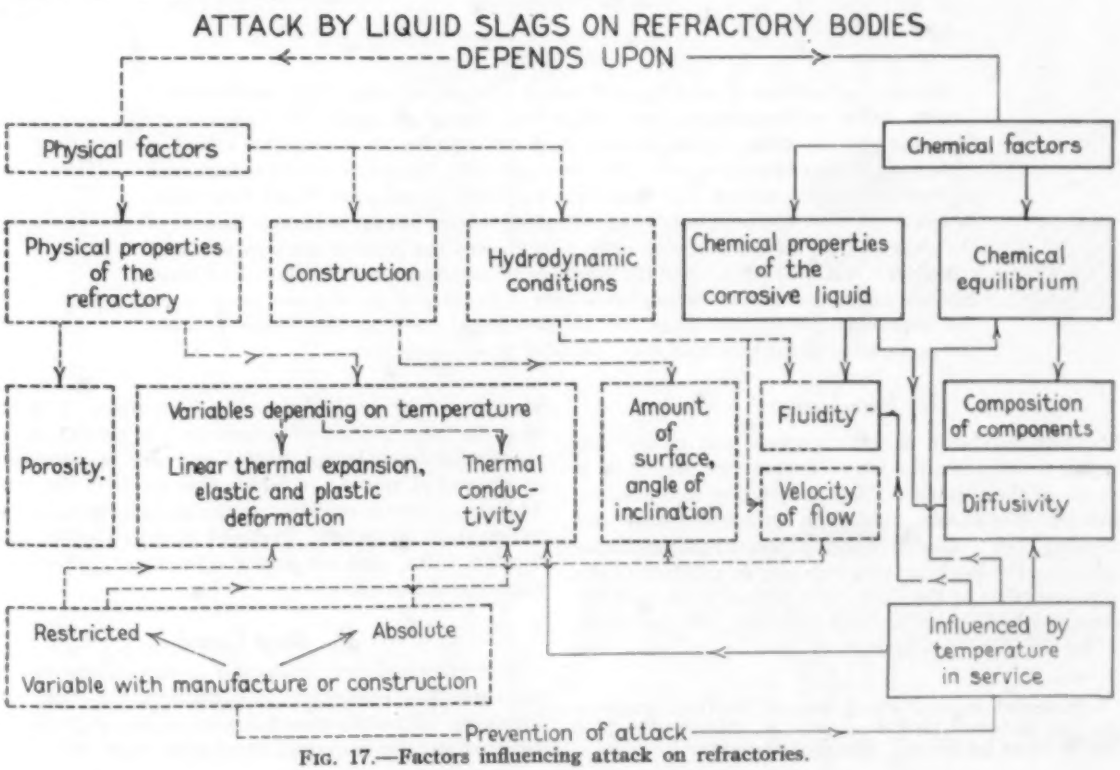

Fig. 17.—Factors influencing attack on refractories.

(3) The results indicate that methods of testing attack by slag or ash should be modified and broadened.

A suggested plan is as follows: (*a*) Determine the solubility of a given refractory in a given slag. When phase data are available, the graphical method used in Fig. 11 is recommended. When such information is lacking, it is necessary to study the melting point of a series of mixtures of slag and refractory. The optical method used by Bro[13] and by Endell and Wens[6] is convenient for this purpose. (*b*) Determine the viscosity of the slag. The methods shown in Figs. 1 and 2 have proved their usefulness and can be safely used. The determination should be carried from the temperature at which the viscosity is 1000 poises to 200°C above the melting point.

VI. Summary

(1) Measurements of the viscosity of slags and glasses and of the action of these molten silicates on a fireclay refractory show that static attack, *i.e.*, attack by a bath of molten material, is nearly independent of the chemical composition of the bath but increases markedly with increasing fluidity of the slag or glass.

(2) An apparatus has been developed to determine the velocity of flow and film thickness of oils as a function of the angle of inclination and width of the path of flow as well as the variation with viscosity and with oil supply. Measurements with this apparatus confirm equations based on established principles of hydrodynamics.

(3) The significance of the results in practical operation is pointed out. Calculations are made to show the influence of viscosity of slag on the velocity of flow and film thickness of some slags and glasses, whose chemical composition and density is known.

(4) A graphical method of determining the solubility of a refractory in a given slag is described.

(5) An analysis of hydrodynamic, thermodynamic, and combustion factors leads to a general equation for slag attack at high temperatures. Viscosity and solubility have a marked influence; combustion conditions, very little influence.

(6) Appreciable resistance to slag attack can be achieved only by selecting a refractory of low solubility in the corroding slag and by reducing the surface temperature of the refractory to less than 50°C above the melting point of the slag in order to build up an unreactive, plastic protective film next to the wall.

[13] Louis Bro, *Chaleur & Ind.*, October, 1933; **18**, 105–14, 172–82, 215–24; (March and May, 1937).

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REACTIONS OF SLAG WITH REFRACTORIES: I, SURFACE REACTIONS *

H. G. Schurecht

Abstract

Several new methods of studying the surface reactions of slags, glass, and Portland cement clinker with refractories were compared. The penetration of the slag into refractories and the slump of slag spheres disclosed considerable information regarding surface reactions which other tests failed to show. For the more refractory slags, such as Portland cement clinker, acid open-hearth, copper reverberatory, and basic open-hearth slags, these reactions were governed largely by the relative acidity or basicity of the slags and the refractories, *i.e.*, basic slags showed the greatest reaction with acid refractories and vice versa. For the more fusible materials, such as glass, lead blast-furnace slag, and coal ash, the relative acidity or basicity of the slag and refractory is less important. With these slags, the low porosity of the refractory, which prevents the penetration of the very fluid slags, probably is more important.

I. Introduction

Surface reactions of slags, glasses, and clinker are known to influence the life of refractories, but little is known of their nature. Slag penetration and reaction with refractories may cause high surface shrinkage and checking, poor structural and thermal spalling resistance, and low load-carrying capacity in addition to the corrosion effect of the slag. The rate of solution of the refractory body ingredients into the slag and the nature of the reaction products may greatly influence the viscosity of the slag and therefore its tendency to penetrate the more porous refractories. The mechanism of these reactions is being studied and will be presented in a series of reports, of which this study is the first. This paper covers research on the surface reactions between slags, glass, and Portland cement clinker with fireclay, silica, and magnesite refractories, using new methods of testing.

II. Slags Tested

The chemical and molecular compositions of the slags used are presented; in calculating the molecular formulas, the metals were taken as oxides, inasmuch as they are usually converted into oxides upon heating.

* Presented at the Fortieth Annual Meeting, American Ceramic Society, New Orleans, La., March 31, 1938 (Refractories Division). Received December 8, 1938.

Basic open-hearth slag

0.307 FeO, .110 MnO, .469 CaO, .114 MgO } 0.031 Al_2O_3 { 0.257 SiO_2, .006 P_2O_5

	(%)
Fe	19.87
P	0.95
Mn	9.92
SiO_2	17.89
Al_2O_3	3.65
CaO	33.30
MgO	5.82
	91.40

Blast-furnace slag

0.888 CaO, .080 MgO, .028 MnO, .004 FeO } 0.164 Al_2O_3 0.630 SiO_2

	(%)
FeO	0.27
MnO	1.78
SiO_2	34.26
Al_2O_3	15.10
CaO	44.94
MgO	2.91
S	1.78
Metal	0.21
	101.25

Portland cement clinker

0.9038 CaO, .0366 MgO, .0596 FeO } 0.0568 Al_2O_3 0.3783 SiO_2

	(%)
SiO_2	21.90
Al_2O_3	5.56
Fe_2O_3	4.58
CaO	65.30
MgO	1.42
SO_3	0.23
Ignition loss	.16
Free CaO	.50
	99.65

Lead blast-furnace slag

0.0021 CuO, .0042 PbO, .4524 FeO, .3636 CaO, .1090 ZnO, .0492 MgO, .0053 BaO, .0139 MnO } 0.0331 Al_2O_3 0.579 SiO_2

	(%)
Cu	0.15
Pb	1.11
SiO_2	32.60
FeO	30.40
S	1.40
CaO	19.10
ZnO	8.30
Al_2O_3	3.12
MgO	1.84
BaO	0.72
MnO	.90
	99.64

Synthetic coal ash

0.027 Na_2O, .040 K_2O, .226 CaO, .301 MgO, .406 FeO } 0.306 Al_2O_3 1.22 SiO_2

	(%)
Na_2O	0.99
K_2O	2.27
CaO	7.56
MgO	7.25
Al_2O_3	18.64
Fe_2O_3	19.36
SiO_2	43.93
	100.00

Soda-lime glass

0.616 Na_2O, .384 CaO + MgO } 0.0163 B_2O_3 2.786 SiO_2

	(%)
SiO_2	74.4
Na_2O	16.9
CaO + MgO	8.2
B_2O_3	0.5
	100.0

Synthetic zinc-furnace slag

0.1098 CaO, .0306 MgO, .3787 ZnO, .4289 FeO, .0520 MnO } 0.0483 Al_2O_3 0.756 SiO_2

	(%)
ZnO	25
FeO	25
MnO	3
CaO	5
MgO	1
Al_2O_3	4
SiO_2	37
	100

Copper-reverberatory slag

0.2337 CuO, .0497 MgO, .0252 ZnO, .0031 BaO, .0078 MnO, .0097 CuO, .0018 PbO, .6694 FeO } 0.040 Al_2O_3 1.096 SiO_2

	(%)
Cu	0.45
Pb	.27
SiO_2	47.40
FeO	34.50
S	0.30
CaO	9.40
ZnO	1.50
Al_2O_3	2.93
MgO	1.44
BaO	0.33
MnO	.40
	98.92

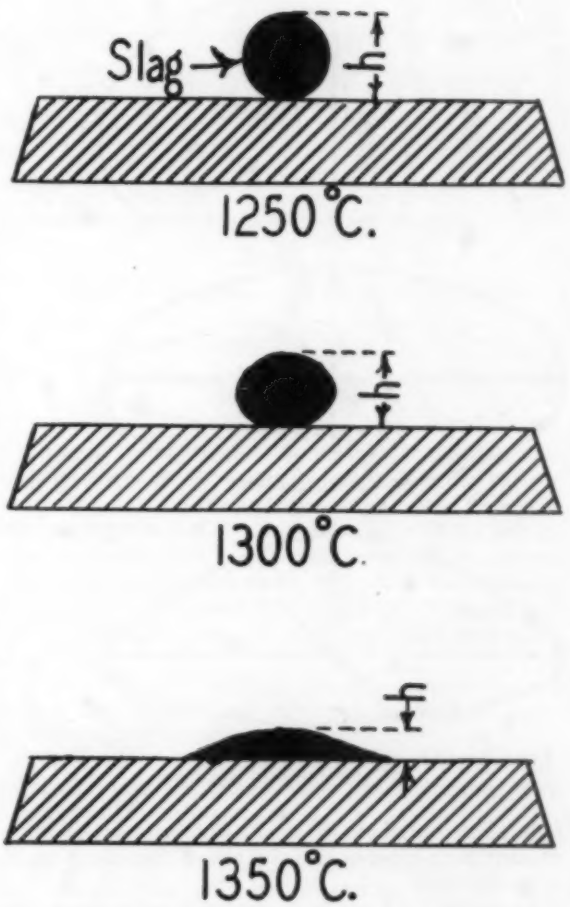

FIG. 1.—Method of testing reactions of slags with refractories.

Acid open-hearth slag

				(%)
0.0687 CaO			SiO_2	58.32
.0327 MgO	0.0531 Al_2O_3	1.565 SiO_2	FeO	22.91
.6034 FeO	.0172 Fe_2O_3		Fe_2O_3	1.44
.2952 MnO			Al_2O_3	2.87
			MnO	11.07
			CaO	2.04
			MgO	0.70
			S	.123
			P_2O_5	.068
				99.541

III. Experimental Methods

The refractory specimens were 3-in. disks, 1/2 in. thick, made of fire clay, ganister, and dead-burned magnesite fired to cone 10, which is a lower temperature than that at which silica and magnesite refractories are ordinarily fired.

The slags were molded into spheres slightly larger than 1/2 inch in diameter. After drying, they were dressed down to size by revolving them in the 1/2-in.

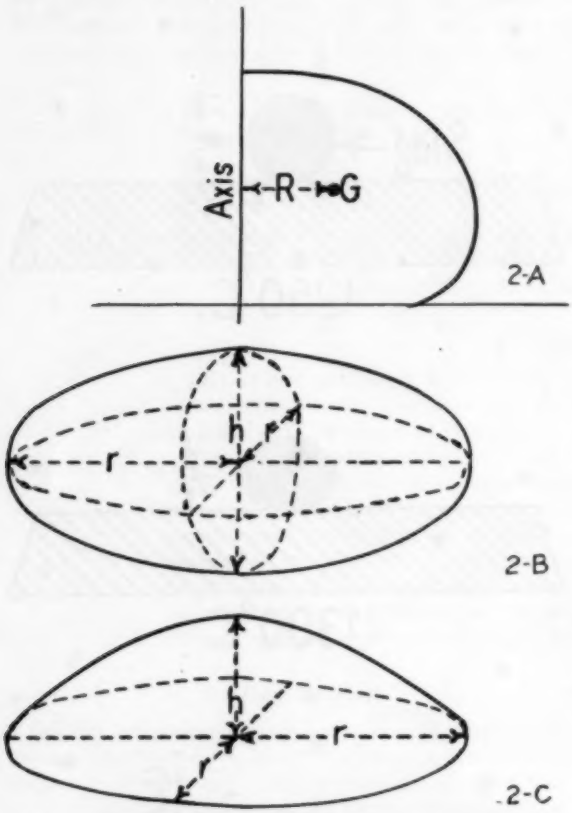

FIG. 2.—(*A*) volume of revolution; (*B*) ellipsoid; (*C*) paraboloidal segment.

hole of a thin sheet of steel. Spheres made in this manner were truer in size and shape than those made by molding only.

In testing the reaction of slags with refractories, the slag spheres were set in the center of the refractory disks (Fig. 1) and fired to temperatures between 850°C and 1450°C in a gas-fired kiln. After firing, the heights and diameters of the slag buttons were measured with an Ames dial and calipers (*h*, Fig. 1). Measurements above the surface were expressed as positive values and those below as negative values. The penetration of the slag into the refractories at first was measured by cutting the refractory specimens in two pieces and noting the depth of penetration. It was found that the penetration, which was evident from the decrease in volume of the buttons, had taken place in some cases but was not visible in the cut sections. This was due to the fact that certain slags did not change the color of the refractories. This confirmed the observations by others that the penetration test[1] generally used in

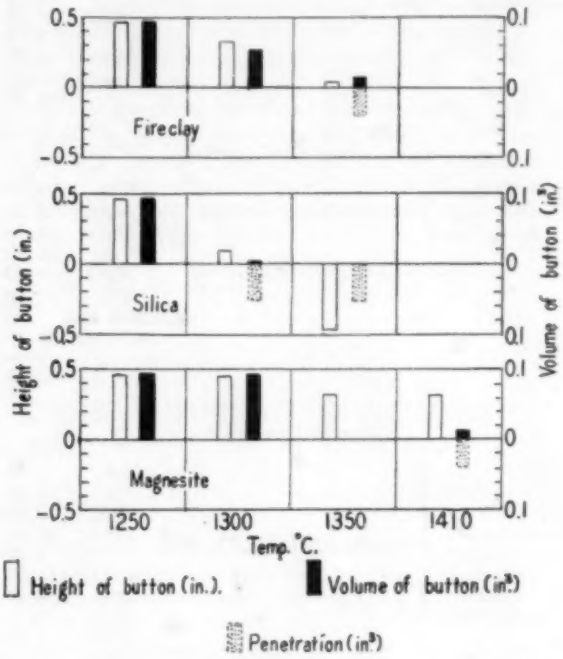

FIG. 3.—Reactions of basic open-hearth slag with refractories.

testing refractories is unreliable. A new method, therefore, was developed by which the penetrations of the slags were calculated from decreases in volume of the slag buttons at different temperatures by means of the following formula:

$$P = (V_1 - S) - V_2. \qquad (1)$$

Where P = penetration (in.³).
V_1 = original vol. of sphere (in.³).
S = shrinkage of sphere in contact with neutral refractory (in.³).
V_2 = vol. of button (in.³).

The volume may be determined by projecting a section of the button on a screen with a delineascope,

[1] C. E. Nesbitt and M. L. Bell, "Practical Methods for Testing Refractory Fire Brick," *Proc. A.S.T.M.*, **16** [Part II], 350–72(1916).

magnifying the specimen about ten times. A planimeter was used to determine the average area of one-half of the sections from the tracings, and the volume was calculated from the following formula (Fig. 2(*A*)):

$$V = 2\pi RA. \quad (2)$$

Where V = vol. of button (in.^{3}).
R = distance of center of gravity (G) from axis (in.).
A = av. area of section of one-half button (in.^{2}).

When the angle of contact was less than 90°, the volume corresponded approximately to that of an ellipsoid calculated from the following formula (Fig. 2(*B*)):

$$V = {}^2/_3\pi r^2 h. \quad (3)$$

Where r = max. radius of button (in.).
h = height of button (in.).

When the angle of contact was greater than 90°, the volume corresponded fairly close to that of a paraboloidal segment calculated from the following formula (Fig. 2(*C*)):

$$V = {}^1/_2\pi r^2 h. \quad (4)$$

It is possible, therefore, to calculate the volume of the slag button to within 5% from its height and average diameter in most cases. The angles of contact of the flattened buttons with the refractories were measured from magnified projections of the buttons by the method employed by Lampman.[3]

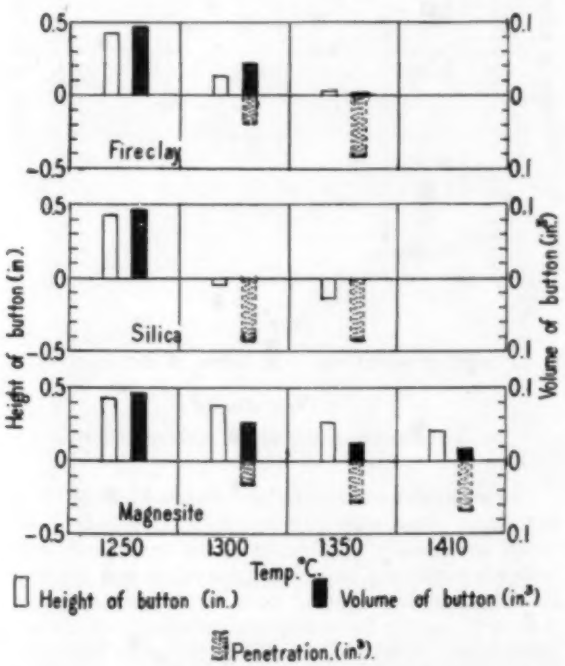

FIG. 4.—Reactions of blast-furnace slag with refractories.

[3] C. M. Lampman, "Flow of Glazes on Flat and Inclined Surfaces," *Bull. Amer. Ceram. Soc.*, **17** [1] 12–16(1938).

IV. Results

The results are given in Figs. 3 to 11.

Judging from changes in heights and volumes of the slag buttons (see Figs. 3 to 6), it is evident that basic open-hearth, blast-furnace, Portland cement clinker, and lead blast-furnace slags reacted more with silica than they did with magnesite brick. In most cases, the reaction with fire clay ranked between that with magnesite and silica brick, but with Portland cement clinker, the reaction with fire clay was greater than it was either with magnesite or silica brick (Fig. 5).

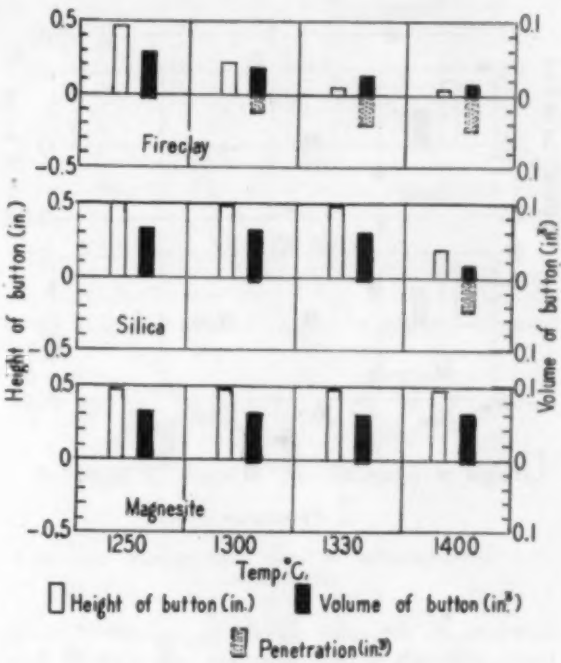

FIG. 5.—Reactions of Portland cement clinker with refractories.

In some instances, the slag button decreased in volume and apparently partially penetrated into the refractory. Upon cutting the specimens in two, however, the penetration did not change the color of the refractory and could not be detected by visual inspection. This was noted particularly with lead blast-furnace slag and magnesite, coal ash and fire clay, coal ash and silica brick, glass and fire clay, and glass and silica brick.

Coal ash, soda-lime glass, and zinc-furnace slag attacked the magnesite and silica brick to about the same extent (Figs. 7, 8, and 9).

Copper-reverberatory and acid open-hearth slags evidently attacked magnesite more than they did silica brick (Figs. 10 and 11).

Portland cement clinker reacted with fireclay brick more than it did with silica and magnesite brick. It also reacted with silica brick more than it did with magnesite brick (Fig. 5).

The slump of the slags on the most slag-resistant refractories for the respective slags is plotted in Fig. 12.

These curves can be used as approximate measurements of their fusibility. The Portland cement clinker was the most refractory, and the glass was the most fusible.

It must be borne in mind that the firing temperature of the silica and magnesite disks (cone 10) is lower than that to which commercial brick are fired; the results,

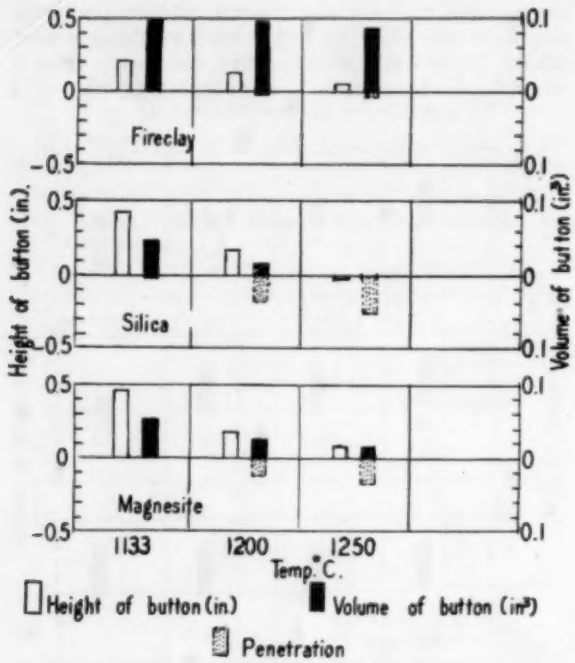

FIG. 6.—Reactions of lead blast-furnace slag with refractories.

therefore, do not apply strictly to commercial refractories, although probably they are fairly close to those which would be obtained with commercial refractories.

V. Discussion of Results

The penetration of the slag into the refractories as measured by visual inspection by the customary penetration test[1] failed to show penetration where it is known to have occurred in some cases. In these instances, the apparent penetration may be calculated from decreases in volume of the slag buttons.

The slump of the spheres, as indicated by their changes in height, gave other significant data. Glasses are probably formed at the contact layer between the slag and refractory. When these glasses were very fluid, they diffused through the slag sphere and reacted further with the slag, which caused them to slump and penetrate into porous refractories. Where no reaction took place or where the reaction products were high-melting viscous glasses, the slag spheres did not slump.

In some instances, the slump of the slag was very marked, but the slag volume did not decrease greatly as in the case of the lead blast-furnace slag on fire clay (Fig. 6). This slag apparently softened considerably, but it did not penetrate into the refractory. With silica brick, however, it not only softened but it also penetrated into the refractory.

Portland cement clinker slumped and became glassy on fire clay when fired to 1300°C; it remained unfused and failed to slump on silica and magnesite brick. Here again, the slump test disclosed a reaction between the slag and body which the old penetration test failed to show.

The penetration of slags into refractories, calculated from the decrease in volume of the slag spheres, and also the slump test disclose evidence of surface reactions which other tests have failed to show.

If it is assumed that slags which slump and decrease in volume the most on magnesite brick are "acid" and those which slump and decrease in volume the most on silica brick are "basic," they may perhaps be roughly classified as shown in Table I.

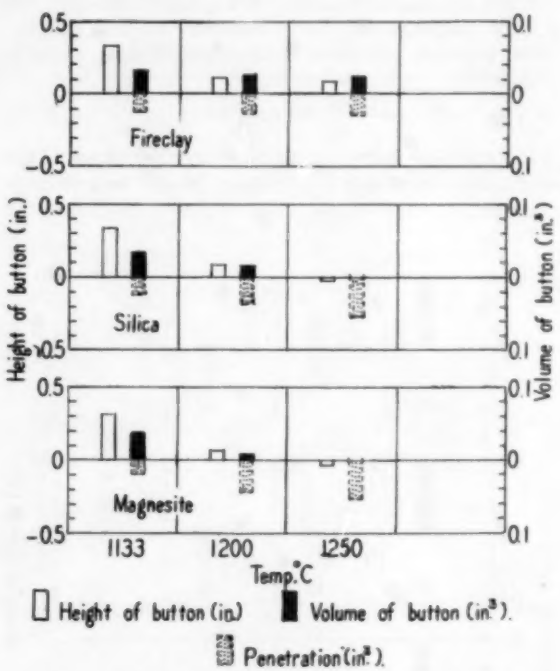

FIG. 7.—Reactions of coal ash with refractories.

The molecular ratios are also tabulated for the different slags. Slags with high SiO_2 to $R_2O_3 + R_2O + RO$ ratios are usually considered to be acid, and those with low ratios are basic. In general, it was apparent that the acid slags reacted most with the basic magnesite brick, and the basic slags reacted most with the acid silica brick. Coal ash, soda-lime glass, and lead blast-furnace slag, however, seem to be exceptions to these rules. These were also the most fusible.

The slump of the slags on the most resistant refractory for each slag may be used as an approximate measure of their fusibility. It must be remembered, however, that even slight reactions between the refractories and slag may somewhat alter the fusibility of these slags. These data are plotted in Fig. 12 for different temperatures. It is apparent that glass, lead blast-furnace

slag, and coal ash are among the most fusible materials tested. In Fig. 13, the relative acidity or basicity of the slags as judged from their reactions with silica and magnesite brick were plotted against their relative fusibilities. The ratios of SiO_2 to $R_2O_3 + R_2O + RO$ were then indicated for each of the slags. For the more refractory and slag. For this type of slag, low porosity and high density of the refractory probably are more important than the relative acidity or basicity of the slag and refractory.

The angle-of-contact method of measuring the wetting ability and slag action corresponds in general with

TABLE I

			$SiO_2:R_2O + RO$	$SiO_2:R_2O_3 + R_2O + RO$	$SiO_2:R_2O_3$
(A)	Basic open-hearth slag	Strongly basic	0.26	0.25	8.29
(B)	Portland cement clinker	" "	0.38	0.36	6.66
(C)	Blast-furnace slag	" "	0.63	0.54	3.84
(D)	Lead blast-furnace slag	Slightly basic	0.58	0.56	17.49
(E)	Coal ash	Neutral	1.22	0.93	3.99
(F)	Soda-lime glass	"	2.79	2.74	17.09
(G)	Zinc-furnace slag	Slightly acid	0.76	0.72	15.65
(H)	Copper-reverberatory slag	" "	1.10	1.05	27.40
(I)	Acid open-hearth slag	Strongly acid	1.57	1.46	22.26

refractory slags (I), (H), (B), and (A), it is apparent that those with high ratios, (I) and (H), reacted more strongly with magnesite than with silica brick. Those with low ratios, (B) and (A), reacted more with silica

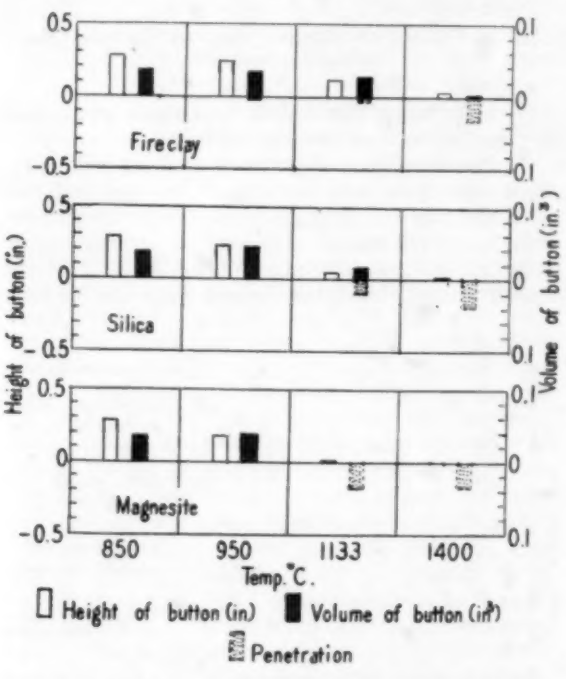

FIG. 8.—Reactions of a soda-lime glass with refractories.

than with magnesite brick. With the more fusible slags, (F), (D), and (E), however, the relation between their ratios and the relative reactions with silica and magnesite brick was not so apparent. It appears, therefore, that the more fusible slags like glass, lead blast-furnace slag, and coal ash reacted almost to the same degree both with magnesite and silica brick. This may be partly due to the fact that their low viscosity permits easy penetration into porous refractories and thereby increases the surface of contact between the

the results obtained by the other tests, but it was not as reliable as the slumping or decrease-in-volume tests.

VI. Summary

(1) New methods of testing the reactions of slags with refractories were compared. The slump and decrease in volume of $^1/_2$-in. spheres of slag resting on the

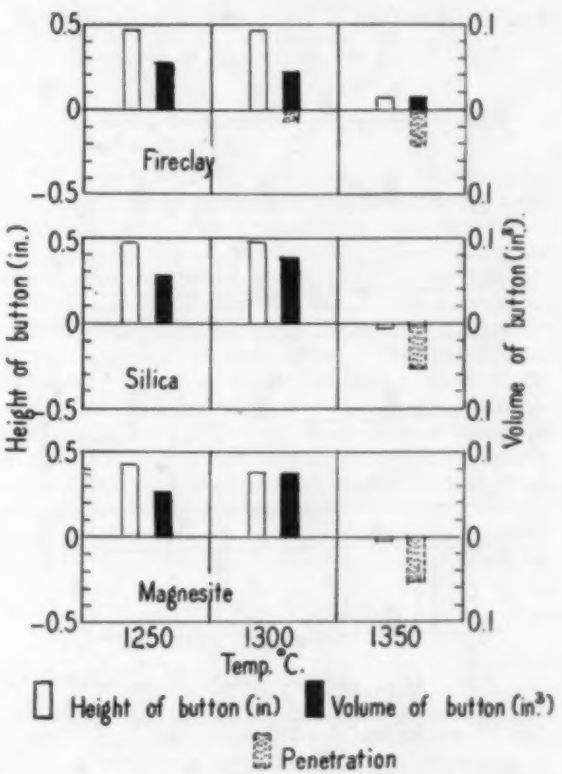

FIG. 9.—Reactions of zinc-furnace slag with refractories.

refractories while they were fired to different temperatures gave more satisfactory results than the old penetration test. The angle-of-contact tests corresponded

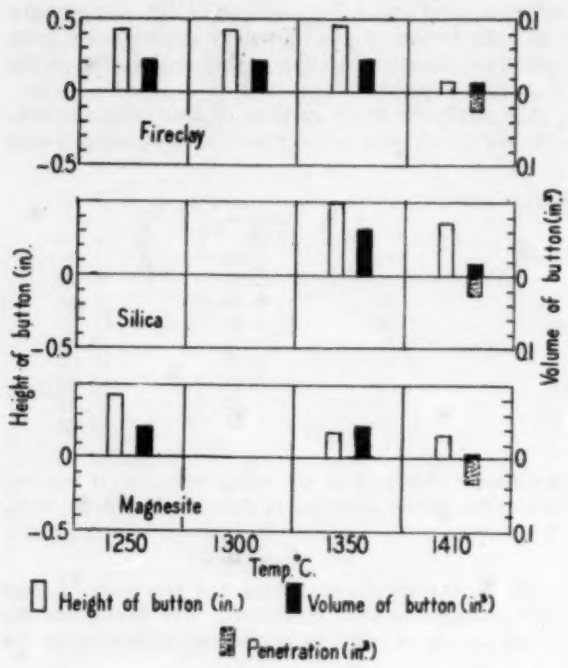

FIG. 10.—Reactions of copper-reverberatory slag with refractories.

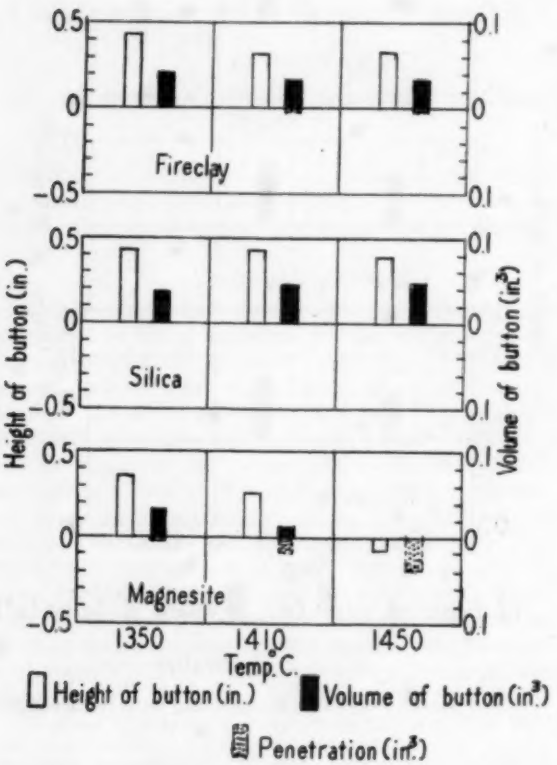

FIG. 11.—Reactions of acid open-hearth slag with refractories.

fairly closely to the other tests, but the results were more difficult to measure.

(2) Measurements of decrease in volume of spheres of slag disclosed penetration of the slag into the refractory, which visual inspection of the sawed specimens failed to show.

(3) Some slags slumped considerably, but they did not penetrate the refractory; others penetrated the refractory but did not slump very much.

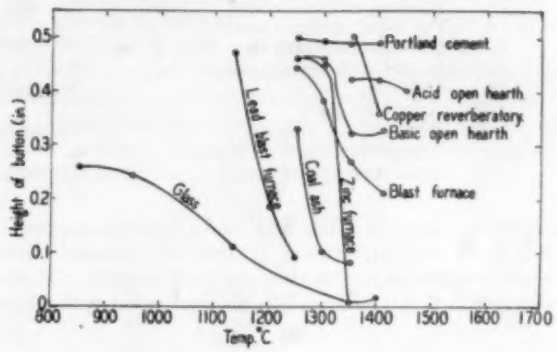

FIG. 12.—Slump of different slags on the most slag-resistant refractories.

(4) Slumping of the slag, in some cases, was caused by reactions between the slag and body.

(5) Assuming that slags which reacted with magnesite more than with silica brick are acid and vice versa and that the slags which react with them to the same degree are neutral, they may be classified apparently as follows: (*a*) basic open-hearth, Portland cement clinker, and blast-furnace slags are strongly

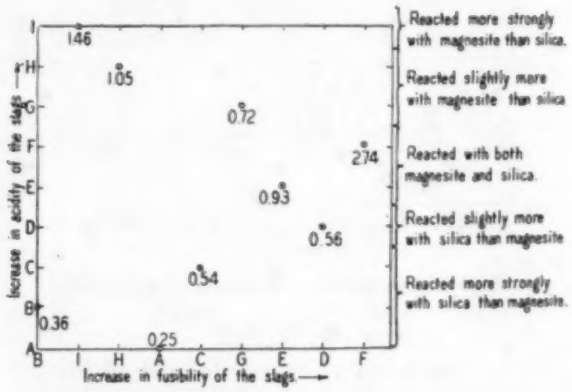

FIG. 13.—Relation between acidity and fusibility of slag and their reaction with refractories (ratio of SiO_2 to $R_2O_3 + R_2O + RO$ indicated).

basic; (*b*) lead blast-furnace slag is slightly basic; (*c*) coal-ash slag and soda-lime glass are neutral; (*d*) zinc-furnace slag is almost neutral, being slightly acid; (*e*) copper-reverberatory slag is slightly acid; and (*f*) acid open-hearth slag is strongly acid.

(6) For the more refractory slags, such as Portland cement clinker, acid open-hearth, copper-reverberatory,

and basic open-hearth slags, the reactions obtained were found to be closely related to the relative acidity or basicity of the slags and refractories, *i.e.*, the acid slag attacked the basic refractories the most severely and vice versa. For the most fusible materials, however, such as glass, lead blast-furnace slag, and coal ash, the slag attacked both acid and basic refractories alike, and the relative acidity or basicity of the slags and refractories appeared to be of minor importance.

Acknowledgment

The writer wishes to acknowledge his indebtedness to M. E. Holmes for helpful suggestions during the progress of the work.

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IDENTITY AND AMOUNTS OF FLUORIDE CRYSTALS PRESENT IN ENAMELS*

By Burnham W. King, Jr., and Andrew I. Andrews

Abstract

A group of enamels containing fluorspar, cryolite, and sodium silicofluoride, added in various proportions, was prepared under carefully controlled conditions, including smelting in an electric resistor furnace. The only mill additions were clay and water; no opacifier was used. X-ray diffraction patterns were made of all the fired enamels. Recrystallized cryolite (Na_3AlF_6), fluorite (CaF_2), and villiaumite (NaF) were found in the fired enamels. Cryolite, the most important opacifier used in the enamels studied, was found to recrystallize whenever enough cryolite or sodium silicofluoride was added in the raw batch. The accuracy of the X-ray method was found to be $\pm 1/2\%$ for villiaumite or fluorite and $\pm 1\%$ for cryolite. A calculation of the unaccounted-for fluorine showed it to be fairly constant at about 2.8%.

I. Introduction

(1) General Discussion

Opaque enamels consist of a clear glass matrix in which particles of different index of refraction than that of the glass are suspended. Owing to this difference in optical properties, light which strikes the particles is scattered. If enough particles are present, most of the light will be scattered and will eventually emerge from the surface of the enamel as diffuse reflection. If this occurs, the enamel is opaque.

From a consideration of the nature of such an enamel, the following factors should determine the reflectance† of an enamel layer, except for what scattering may take place at the enamel surface: (1) quantity of the scattering material; (2) thickness of the enamel layer; (3) difference in refractive index between the scattering material and the glass matrix; (4) particle size of the scattering material; (5) distribution of the scattering material; (6) absorption characteristics of the scattering material and the glass matrix; and (7) wave-length of the incident light.

(2) Object of Study

The object of this study was to investigate the fundamental characteristics of the opacity of sheet-iron cover enamels. Upon considering the methods of producing opacity, it was seen that the two ways of adding opacifiers are as additions (1) to the frit composition and (2) to the mill batch. All satisfactory opaque white enamels have an opaque frit, irrespective of what mill additions are added. The investigation of opacity, therefore, was begun with a study of frit opacifiers. The materials most commonly used for this purpose are fluorides and compounds of antimony. Because fluorides are present in practically all cover-coat frits, it was decided to study the enamels in which they are the only opacifying agents.

The literature references, which were used as a review background for this study, are given in a Bibliography on p. 132.

II. Procedure

(1) Preparation of Enamel Batches

The base enamel selected for investigation was one of fairly typical composition and one on which considerable work had been done at the University of Illinois. Fluorides, which were used to produce opacity, were added as fluorspar, cryolite, and sodium silicofluoride. Fifteen enamel batches of the compositions given in Table I were prepared; these compositions are shown graphically in Fig. 1. The materials used were chiefly of commercial purity.

* Presented at the Fortieth Annual Meeting, American Ceramic Society, New Orleans, La., March 31, 1938 (Enamel Division). Received March 31, 1938.

Based on thesis submitted by Burnham W. King, Jr., in partial fulfillment of the requirements for the degree of Ph.D. in Engineering, University of Illinois, February, 1938.

† Reflectance is the fraction of incident light reflected from a specimen. From "Tentative Definitions of Porcelain Enamel Terms," Porcelain Enamel Institute, Inc., January, 1936.

The various mixtures were made in 400-gram batches. To assure satisfactory uniformity, all materials were screened through a No. 20 screen and were mixed thoroughly on a large sheet of paper. As far as possible, all batches were made at the same time to avoid variations in moisture content. The degree of hydration in the borax was checked by titration, and suitable allowance was made in the batch compositions, which are given for borax of the composition $Na_2B_4O_7 \cdot 10\ H_2O$.

TABLE I

RAW BATCH COMPOSITIONS IN PER CENT*

Series A Enamel No.	Cryolite (%)	Fluorspar (%)	Sodium silico-fluoride (%)
1	17	0	0
2	13	4	0
3	13	0	4
4	9	8	0
5	9	4	4
6	9	0	8
7	5	12	0
8	5	8	4
9	5	4	8
10	5	0	12
11	0	17	0
12	0	12.5	4.5
13	0	8.5	8.5
14	0	4.5	12.5
15	0	0	17

* To each enamel batch composition, the following materials were added: feldspar 30%, borax 26%, quartz 20%, soda ash 4%, and soda niter 3%; all materials were of known purity.

(2) Smelting

All batches were smelted in fireclay crucibles just large enough for a 400-gram batch. A vertical electric resistor furnace† with a Smith alloy winding was used for the smelting. The furnace and batch temperatures were measured with Chromel-Alumel thermocouples, and the furnace temperature was automatically controlled and recorded by a Leeds and Northrup recording potentiometer. The Chromel-Alumel couples were checked with a standard platinum couple. The regular smelting procedure consisted of placing an empty crucible in the furnace and raising the furnace temperature to 2200°F; then the crucible was removed, charged with 400 grams of batch, and returned to the furnace as soon as possible. The controller was set for the desired smelting temperature. The enamel batch was smelted, stirred thoroughly, and after ten minutes removed from the furnace. All frits were quenched in water and dried before milling.

In order to determine a good smelting procedure, a number of batches of enamel No. A-5 (Table I) was made and smelted at different temperatures for different lengths of time. The molten enamels were quenched, milled, sprayed, and their reflectance was determined according to the procedure given in section II (6). For enamel No. A-5, a smelting schedule of one hour at 2100°F was found to give the best reflectance. All fifteen enamel compositions were then made using this schedule.

† Donated by Hevi Duty Electric Co., Milwaukee, Wis.

(3) Milling

Two hundred and fifty grams of frit were used in the mill batches. The mill additions were frit 100, clay 5, and water 60 parts.

Vallendar clay and distilled water were the only mill additions used in order to avoid the effect which the usual electrolytes or mill-added opacifiers would have on the reflectance. The batches were ground for 3000 revolutions in 8-inch porcelain ball mills, giving a fineness of about 10 grams residue from 100 grams of frit on a No. 200 screen. As soon as the enamels were milled, they were screened through a No. 40 screen, placed in glass jars with rubber seals, and allowed to stand for at least 24 hours before being applied.

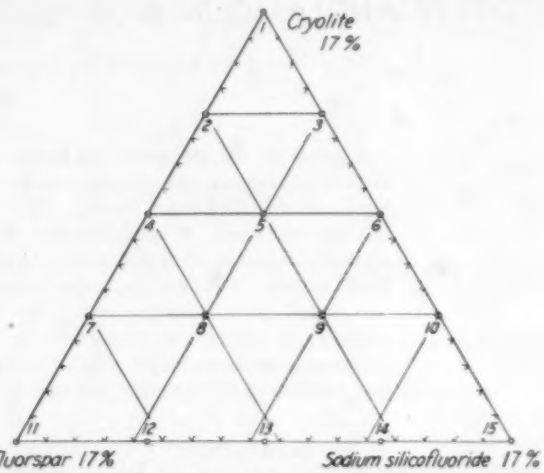

FIG. 1.—Frit batches for A-series enamels. Batch composition: feldspar 30, borax 26, quartz 20, soda ash 4, soda niter 3, total 83%; fluorides 17%.

(4) Application

Samples for the reflectance tests were prepared by spraying the milled enamel on previously weighed 4-in. square ground-coated pieces of sheet iron. To obtain a uniform coating, the pieces were sprayed to a definite wet weight, dried, and brushed to leave an area of 12 sq. in. of white enamel. The enamel was then fired and the piece was weighed. Two uniform coats were applied, giving a total fired weight of 72 grams per sq. ft., but before applying the second coat, a correction (if necessary) was made in the wet weight of this coat so that the proper fired weight could be obtained for the two coats. The technique of spraying was standardized, and the enamel was applied as uniformly as possible. When the final dried weight was correct to within ± 0.2 gram, the piece was fired.

(5) Firing

The pieces were fired on alloy points in a small electric resistor furnace with a 7- by 12-in. hearth. The temperature, which was automatically regulated by a

potentiometer controller, was checked from time to time with a standard platinum couple. A firing schedule of $2^1/_2$ minutes at 1500°F was used, which gave a good gloss and no signs of overfiring. When the pieces were removed from the furnace, they were placed on a rack and allowed to cool in the air. The heating and cooling schedule was thus carefully controlled to assure uniformity of heat treatment.

(6) Reflectance Tests

When the pieces were cool, their reflectance was measured with a Hunter reflectometer which was calibrated with standards provided by the National Bureau of Standards. Readings were taken both for the first and for the second coats.

(7) Outline of Method Followed in X-Ray Analysis

The method of X-ray analysis used was essentially that described by Clark and Reynolds[1] for the analysis of mine dust. Minor changes were necessary to adapt the method to the analysis of enamels. The following method was used:

(1) Standards were prepared, containing known weights of crystalline material and glass covering the variations expected in the sample to be analyzed. In addition, 10% of magnesium oxide was added to serve as a reference for intensity measurements.

(2) The same proportion of reference material as that added to the standards was also added to the samples to be analyzed.

(3) All samples were finely ground and X-ray patterns were taken. The same time of exposure and the same development of the films were used, although excessive care was unnecessary because all intensity measurements were made relative to the reference material.

(4) Microphotometer curves were made of all patterns. By comparing the intensities of the lines of the various crystalline materials with the intensity of nearby lines of the reference material, ratios of intensities were obtained both for the standards and for the unknown samples. The ratios obtained with unknown samples were then compared with those from the standard samples, and the amounts of crystalline materials present in the unknowns were determined.

(8) Preparation of Standards for X-Ray Analysis

The glass used in the X-ray standards was of the same composition as the enamels, except that no fluorides were added. The glass was fritted, quenched in water, powdered, and ground. An X-ray picture of a typical sample showed only a faint trace of quartz.

The materials used for the standards were chemically pure sodium fluoride and magnesium oxide, commercial Greenland cryolite, and a single optically clear fluorite crystal. The coarse materials were crushed in a steel mortar, and the iron was removed with an electromagnet. All materials were dried at 110°C before being weighed. To insure uniformity of composition and a satisfactory fineness, all standards were mixed with alcohol and were ground for 24 hours in a small glass mill with agate balls. The loss from these balls during grinding was only about 0.001 gram per hour. After the mill grinding was completed, the alcohol was volatilized, and the sample was ground in an agate mortar. Materials receiving this treatment were reduced to a particle size sufficiently fine to give the smooth lines in an X-ray diffraction pattern which were necessary to obtain an accurate X-ray analysis.

(9) Preparation of Samples for X-Ray Analysis

Because some difficulty was encountered in obtaining large enough samples from the enameled pieces used in the reflectance tests, special samples were prepared for X-ray analysis. A relatively thick layer of enamel was applied over a small area on the standard 4-in. ground-coated pieces. The enamel was then dried, fired, and cooled in the usual manner. A second coat was also applied and given the same treatment. This gave a layer of enamel thick enough to be chipped off readily. The enamel thus obtained was ground in a steel mortar to pass a No. 60 screen, and the iron was removed with an electromagnet. A sample of approximately one gram was accurately weighed, and to this 10% of dry magnesium oxide was added. The materials were then ground in the glass ball mill and were dried (see Section II (8)).

(10) Method for Making X-Ray Diffraction Patterns

The sample was mounted in the form of a wedge at the center of a circular camera, and a film was placed around the circumference of the camera, which was 6.38 cm. in radius. A tube with a copper target operating at 30 kv. and an average filament current of 23 ma. was used to provide the X-ray beam which was passed through the powdered sample. Patterns could be obtained in 15 hours from enamels containing crystalline material. Unfiltered K-alpha radiation was used. The X-ray beam was not strictly monochromatic in that beta lines appeared for all the strong lines in a pattern. This, however, was deemed less objectionable than the fogging, which would have occurred with the longer exposures necessary with a filter.

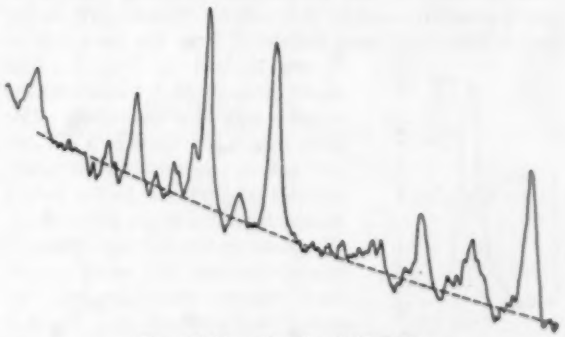

FIG. 2(*A*).—Standard No. 13.

(11) Microphotometer Curves

Curves showing the intensity of darkening of the photographic film were obtained with a microphotometer, an instrument in which a beam of light is passed

[1] See reference (22) in Bibliography, p. 133.

through the slowly moving X-ray film and focused on a thermopile. The thermopile actuates a galvanometer to which a small mirror is fastened. A second beam of light shines on the mirror and is reflected onto a revolving drum covered with light-sensitized paper. Dark lines on the X-ray pattern appear as peaks in the curve traced by the beam of light on the sensitized paper. By synchronizing the motion of the film and the rotation of the drum, the distances between the peaks were made proportional to the distances between the lines on the X-ray pattern.

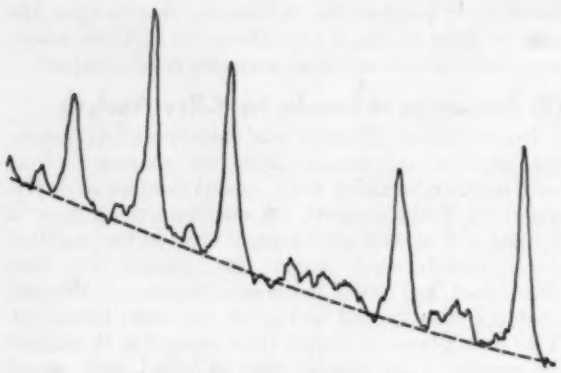

FIG. 2(*B*).—Enamel No. A-5.

The first step in measuring the microphotometer curves was the approximation of a base line (dotted lines in Figs. 2 and 3). This base-line curve shows the darkening of the photographic film, due to the glass present in the sample, and the lines of the X-ray diffraction patterns of the crystalline materials appear as peaks superimposed on this curve. The heights of the peaks, therefore, were measured from the base line as shown by (*h*) in Fig. 3. The width (*w*) at half maximum intensity was also measured. The intensity of the lines in an X-ray diffraction pattern were considered proportional to the height times the width of the corresponding peaks on the microphotometer curve, because the most consistent results were obtained by using this product as a basis of comparison. By measuring the width as well as the height, some correction was afforded for variations in line widths due to differences in the particle size of the crystalline materials; *e.g.*, for sizes below 10^{-6} cm., the smaller the particle the greater the width (*w*) of the line. The base line from which (*h*) was measured had to be approximated from the general shape of the intensity curve.

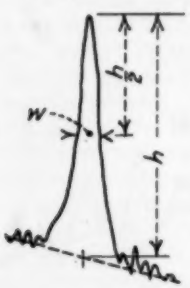

FIG. 3.

(12) Preparation of Samples for Microscopic Examination

Thin sections for microscopic examination were made according to the usual petrographic technique for the preparation of rock sections, except that the sections were made thinner. This was done by giving the sample a final grinding on a glass plate, using levigated alumina suspended in a soap and water solution. The sections were cut diagonally through the enamel layer to give a larger area for observation.

III. Results

(1) Reflectance Data

The reflectance data were obtained according to the method outlined in the procedure. To obtain average values for the reflectance at 72 grams per sq. ft., all values of reflectance for various weights of enamel for a given sample were plotted, and the desired value was taken from the curve.

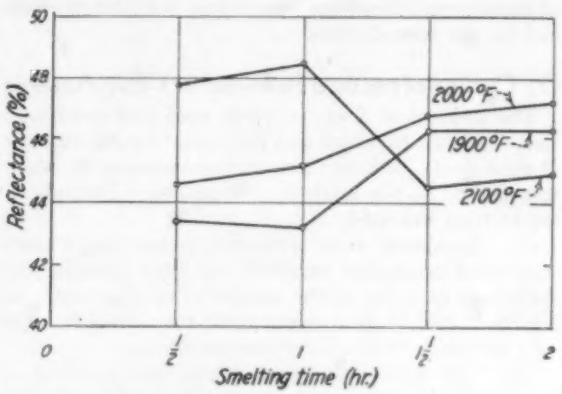

FIG. 4.—Reflectance *vs.* smelting time and temperature for fired weight of enamel at 72 g. per sq. ft.

The results of the study of the effect of smelting time and temperature on reflectance are shown in Fig. 4. It is seen that for the enamel composition used and the heat treatment it received in smelting, fritting, and in the subsequent firing and cooling of the enamel piece, a smelting schedule of one hour at 2100°F gave the highest reflectance. The results obtained for the A-series of enamels are given in Fig. 5.

TABLE II

COMPOSITIONS OF STANDARDS FOR X-RAY ANALYSIS

Standard No.	NaF (g.)	CaF_2 (g.)	Cryolite (g.)	Glass (g.)	MgO (g.)
1	0.100	0.000	0.000	0.900	0.100
2	.075	.025	.000	.900	.100
3	.050	.050	.000	.900	.100
4	.025	.075	.000	.900	.100
5	.000	.100	.000	.900	.100
6	.200	.000	.000	.800	.100
7	.150	.050	.000	.800	.100
8	.100	.100	.000	.800	.100
9	.050	.150	.000	.800	.100
10	.000	.200	.000	.800	.100
11	.000	.000	.100	.900	.100
13	.000	.050	.050	.900	.100
14	.000	.050	.150	.800	.100
15	.000	.150	.050	.800	.100

(2) X-Ray Data

Table II gives the compositions of the standards prepared for quantitative X-ray analysis. X-ray patterns were obtained for these standards and for the various enamels to be studied.

Microphotometer curves, such as those shown in Figs. 2 (*A*) and (*B*), were made of all X-ray patterns. It was found that the best section of the film to cover was that 3.5 to 7.5 cm. from the central spot, because

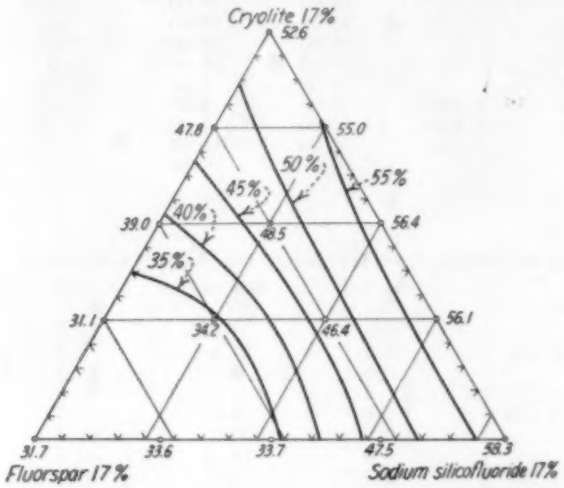

FIG. 5.—Per cent reflectance *vs.* batch composition for fired weight of 72 g. per sq. ft. Batch composition: feldspar 30, borax 26, quartz 20, soda ash 4, soda niter 3, total 83%; fluorides 17%. Mill additions: frit 100, clay 5, and water 60 parts.

it included the lines which could best be measured. These lines occurred at 4.32, 4.79, 5.23, 6.23, and 6.94 cm. from the central spot. Of these, the lines at 4.79 and 6.94 were those of the MgO reference material, and the others were from the fluorides. The height (h) and the width (w) were determined for all of these lines and from them their product (p). The products were numbered p_1, p_2, p_3, p_4, and p_5, respectively, for these five lines. Because the intensities are proportional to these products, the ratio of two products may be used as the ratio of the intensities of their respective lines. Thus the intensities of the lines at 4.32 and 5.23 were compared with that of the MgO line at 4.79, and the ratios, p_1 to p_2 and p_3 to p_2, were obtained. The intensity of the line at 6.23 was compared with that of the MgO line at 6.94, and the ratio p_4 to p_5 was thus obtained. The average values of the intensity ratios, p_1 to p_2, p_3 to p_2, and p_4 to p_5, and the percentages of crystalline materials are given for the patterns of the standards in Table III. The same information for patterns taken on the A-series of enamels are given in Table IV.

In the analysis of the data, some difficulty arose, owing to the presence of coincident or partially coincident lines in the X-ray patterns. As mentioned before, unfiltered radiation was used; therefore beta lines were present as well as those from the much stronger alpha doublet. In some cases, the beta line for one material conflicted with the alpha line for another material; there was also some coincidence between the strong lines of the various fluorides. The locations of the various lines considered in this investigation are shown in Table V. All distances were measured from the central spot. The values given are those calculated from crystallographic data as well as those obtained by actual measurement of X-ray patterns. The agreement appears to be good, indicating that the Miller indices given are probably correct. It is to be noted that the lines falling at about 4.32 cm. from the central spot could not be separated on the microphotometer curve. The same is true with those at about 6.23 cm. The 220-beta line of CaF_2 and the 220-beta

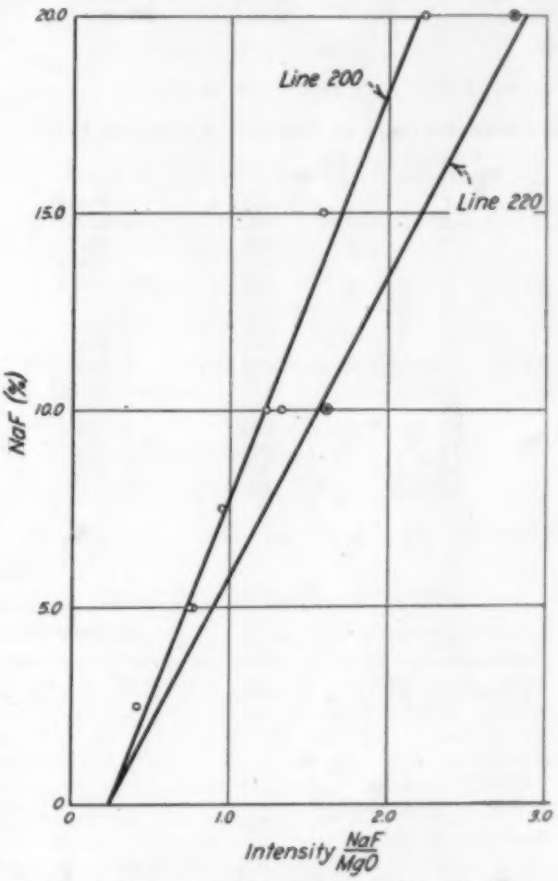

FIG. 6.—Per cent villiaumite (NaF) *vs.* intensity ratio.

of cryolite, which were practically coincident, could be distinguished from the 200-alpha of MgO, although a slight correction was sometimes necessary in the widths of the peaks. In making measurements on the microphotometer curves, distinctions such as these were made wherever possible, and the lines which could not be separated were dealt with as single lines. In this way, the products, p_1, p_2, p_3, p_4, and p_5, were obtained.

From the ratios, p_1 to p_2, p_3 to p_2, and p_4 to p_5, for the X-ray patterns of the standards, it was possible to

TABLE III

AVERAGE VALUES OF INTENSITY RATIOS AND PERCENTAGES OF CRYSTALLINE MATERIALS FOR STANDARDS

Standard No.	p_1/p_2	Amount of p_1/p_2 due to cryolite alone	p_3/p_2	Amount of p_3/p_2 due to cryolite alone	p_4/p_2	Villiaumite (NaF) (%)	Fluorite (CaF_2) (%)	Cryolite (%)
1	1.322		0.000		1.614	10.00	0.00	0.00
2	0.947		0.475			7.50	2.50	0.00
3	0.766		1.010			5.00	5.00	0.00
4	0.406		1.284			2.50	7.50	0.00
5	0.000		1.728		1.080	0.00	10.00	0.00
6	2.238		0.000		2.790	20.00	0.00	0.00
7	1.577		0.973			15.00	5.00	0.00
8	1.225		1.822			10.00	10.00	0.00
9	0.745		2.590			5.00	15.00	0.00
10	0.000		3.293		1.737	0.00	20.00	0.00
11	0.336	0.111	0.346	0.346		0.00	0.00	10.00
13	0.281	0.056	1.069	0.119	0.439	0.00	5.00	5.00
14	0.431	0.206	1.389	0.439	0.443	0.00	5.00	15.00
15	0.316	0.091	2.669	0.119	1.294	0.00	15.00	5.00

TABLE IV

AVERAGE VALUES OF INTENSITY RATIOS AND PERCENTAGES OF CRYSTALLINE MATERIALS FOR A-SERIES ENAMELS

A-Series Enamel No.	$p_1/p_2 = A$	$p_3/p_2 = B$	$p_4/p_2 = C$	Villiaumite (%)	Fluorite (%)	Cryolite (%)
1	0.450	0.484		0.3	0.0	15.0
2	.362	0.925	0.561	0.2	3.9	9.3
3	.424	0.483		0.0	0.0	15.0
4	.050	1.558	1.240	2.4	9.0	3.8
5	.548	1.048	0.800	1.8	4.3	11.4
6	.391	0.470		0.0	0.0	14.7
7	.237	2.015		0.0	11.7	0.0
8	.534	1.413	1.208	2.7	8.1	3.9
9	.368	1.019	0.525	0.0	4.0	12.0
10	.417	0.472		0.0	0.0	14.7
11	.269	2.310		0.3	13.5	0.0
12	.298	2.034	1.251	0.5	12.3	2.7
13	.369	1.634	1.066	0.9	9.3	4.7
14	.365	1.168	0.610	0.0	5.0	11.5
15	.420	0.486		0.0	0.0	15.0

TABLE V

LOCATION OF FLUORIDE AND MAGNESIUM OXIDE LINES IN X-RAY PATTERNS*

Calculated values								Measured values (Position, cm.)
NaF		CaF_2		Cryolite		MgO		
Indices	Position (cm.)	Indices	Position (cm.)	Indices	Position (cm.)	Indices	Position (cm.)	
		111	3.17					3.17
				200†	3.27†			
				200	3.60			3.63
200†	3.89†			211†	3.89†			3.89
200	4.35			211	4.35	200†	4.31†	4.32‡
		220†	4.70†	220†	4.68†			4.68
						200	4.79	4.79‡
		220	5.25	220	5.22			5.23‡
220	6.23	113	6.18			220†	6.20†	6.23‡
						220	6.95	6.94‡

* All values are for copper radiation and a circular camera 6.38 cm. in radius.
† Lines for beta radiation; the remainder for alpha radiation.
‡ Lines measured for X-ray analysis.

plot curves showing the percentage of NaF or CaF_2 as a function of the ratio of the intensity of a given line in the fluoride pattern to that of one in the MgO pattern. Curves for NaF and CaF_2 are shown in Figs. 6 and 7. The curves for the lines of NaF and the 113-line of CaF_2 do not pass through the origin; they intersect the intensity ratio axis at 0.225. This is the effect of the superposition of MgO-beta lines, but because the same percentage of MgO is present in all samples and the ratio of intensity of alpha-to-beta lines is constant, the correction for the MgO-beta lines will be a constant, which is equal to a ratio of 0.225.

In the case of standards Nos. 13, 14, and 15, containing both CaF_2 and cryolite, the 220-lines of the two materials are coincident. In this case, the amount of the intensity ratio due to CaF_2 was determined

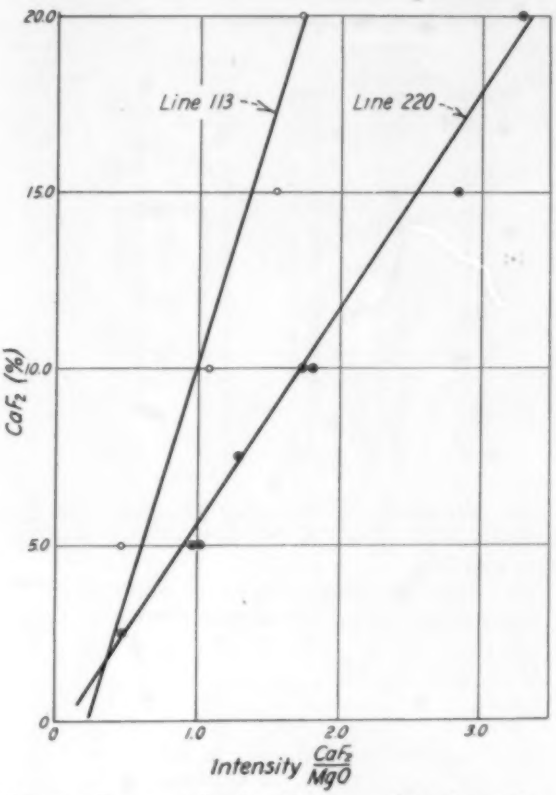

FIG. 7.—Per cent fluorite (CaF_2) *vs.* intensity ratio.

from the curve already plotted (Fig. 7), and the amount of the ratio due to the cryolite was obtained by difference. Figure 8 shows the percentage of cryolite as a function of the intensity ratio.

If only one crystalline material were present in an enamel sample, its amount could be determined directly from the standard curve for that material. If two materials were present, they could probably be determined by lines in the two patterns which did not conflict. If three materials were present and their strong lines coincide, as is the case with the fluorides, the quantities of each could not be determined directly.

From an inspection of the curves in Figs. 6 to 8, it is seen that the intensity ratio is a straight-line function of the composition. In the case of a line whose intensity is due to the sum of several coincident lines, a linear equation may therefore be set up, showing the amount contributed by each material. This had to be done in the case of most of the enamel samples, owing to the superposition of the strong lines of the various fluorides. The method of calculation is as follows:

If x = % NaF.
y = % CaF_2.
z = % cryolite.

Then m_1 = reciprocal of slope of curve for NaF 200 line (Fig. 6).
m'_1 = " " " " " " " " 220 " (Fig. 6).
m_2 = " " " " " CaF_2 220 " (Fig. 7).
m'_2 = " " " " " " " " 113 " (Fig. 7).
m_3 = " " " " " " cryolite 211 " (Fig. 8).
m'_3 = " " " " " " " " 220 " (Fig. 8).

If the ratio of intensities due to MgO-beta lines equals 0.225, and intensity ratios, p_1 to p_2, p_3 to p_2, and p_4 to p_2, equal A, B, and C, respectively, then the following equations can be written:

$$m_1x + m_3z + 0.225 = A. \quad (1)$$

$$m_2y + m'_2z = B. \quad (2)$$

$$m'_1x + m'_2y + 0.225 = C. \quad (3)$$

The values of m obtained from Figs. 6 to 8 are as follows:

$m_1 = 0.098.$ $m'_1 = 0.132.$
$m_2 = 0.160.$ $m'_2 = 0.078.$
$m_3 = 0.0125.$ $m'_3 = 0.032.$

Substituting these values for m in equations (1), (2), and (3), the following equations are obtained:

$$0.098x + 0.0125z + 0.225 = A. \quad (4)$$
$$0.16y + 0.032z = B. \quad (5)$$
$$0.132x + 0.078y + 0.225 = C. \quad (6)$$

The solution of these equations in the case of enamel No. A-5 is as follows:

Enamel No. 5

$$0.098x + 0.0125z - 0.225 = 0.548.$$
$$0.16y + 0.32z = 1.048.$$
$$0.132x + 0.078y + 0.225 = 0.800.$$

The solution of these equations gives the following values:

$$x = 1.83\%. \quad y = 4.26\%. \quad z = 11.44\%.$$

The summarized results of the X-ray analysis are given in Table IV and in Figs. 9, 10, and 11, where they are plotted in triaxial form on the basis of the batch compositions. The X-ray analysis results, because they are for the fired enamel, are on the basis of the melted composition. To determine how the results of the X-ray analysis might compare with the maximum possible crystalline material obtainable from the various enamels, the melted composition for each enamel was calculated, assuming no loss of fluorine by volatilization. These results are given in Table VI.

(3) Results of Microscopic Examination

The following results were obtained by a microscopic examination of the thin sections of enamels Nos. A-1, A-5, A-11, and A-15. Enamel No. A-1 had an average particle size of approximately $^1/_2$ micron. The size of the particles in enamel No. A-15 appeared slightly smaller. In both of these enamels, the particles appeared to be of nearly uniform particle size. Enamel No. A-15 showed a mixture of particle sizes; it contained a few large particles, 5 to 10 microns, and a

background of very fine material which could not be resolved sufficiently to be measured even approximately. Enamel No. A-5 was a mixture of the three end members just described, but it resembled enamel No. A-1 most closely. Enamel No. A-11 apparently was the most viscous of the enamels; it contained the largest bubbles and the boundaries of the original frit grains appeared to be the least disturbed. On the other hand, enamel No. A-15 appeared to be the most fluid because the boundaries of the frit grains were much less distinct and the bubbles were smaller.

TABLE VI

CALCULATION OF FLUORIDE CONTENT ON BASIS OF MELTED COMPOSITION

A-Series Enamel No.	CaF_2 (%)	Na_2SiF_6 (%)	Cryolite (%)	Maximum possible cryolite from Na_2SiF_6 (%)	Total possible cryolite (%)	Difference between theoretical and actual cryolite (%)	Fluorine in this cryolite (%)	Difference between theoretical and actual CaF_2 (%)	F in this CaF_2 (%)	Total F from cryolite and CaF_2 (%)	F in actual NaF (%)	Total F not accounted for in X-ray analysis (%)
1	0.0	0.0	19.4	0.0	19.4	4.4	2.4	0.0	0.0	2.4	0.1	2.3
2	4.5	0.0	14.8	0.0	14.8	5.5	3.0	0.6	0.3	3.3	0.1	3.2
3	0.0	4.5	14.8	5.0	19.8	4.8	2.6	0.0	0.0	2.6	0.0	2.6
4	9.1	0.0	10.2	0.0	10.2	6.4	3.5	0.1	0.0	3.5	1.1	2.4
5	4.5	4.5	10.2	5.0	15.2	3.8	2.1	0.2	0.1	2.2	0.8	1.4
6	0.0	9.1	10.2	10.2	20.4	5.7	3.1	0.0	0.0	3.1	0.0	3.1
7	13.7	0.0	5.7	0.0	5.7	5.7	3.1	2.0	1.0	4.1	0.0	4.1
8	9.1	4.5	5.7	5.0	10.7	6.8	3.6	1.0	0.5	4.1	1.2	2.9
9	4.5	9.1	5.7	10.2	15.9	3.9	2.1	0.5	0.2	2.3	0.0	2.3
10	0.0	13.7	5.7	15.3	21.0	6.3	3.4	0.0	0.0	3.4	0.0	3.4
11	19.4	0.0	0.0	0.0	0.0	0.0	0.0	5.9	2.9	2.9	0.1	2.8
12	14.2	5.1	0.0	5.7	5.7	3.7	2.0	1.9	0.9	2.9	0.2	2.7
13	9.7	9.7	0.0	10.8	10.8	6.1	3.3	0.3	0.1	3.4	0.4	3.0
14	5.1	14.2	0.0	15.9	15.9	4.4	2.4	0.1	0.0	2.4	0.0	2.4
15	0.0	19.4	0.0	21.7	21.7	6.7	3.6	0.0	0.0	3.6	0.0	3.6

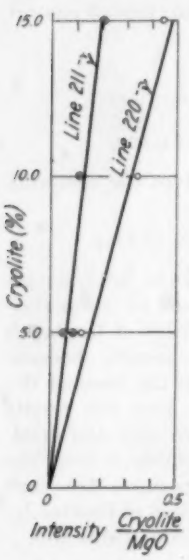

FIG. 8.—Per cent cryolite *vs.* intensity ratio.

IV. Discussion of Results

In the introduction, it was stated that, aside from the scattering of light due to surface roughness, the reflectance of an enamel layer is due to seven factors. These factors and the manner in which they were studied may be outlined as follows:

(*1*) *Quantity of Scattering Material:* The quantity of crystalline material was determined by X-ray analysis, supplemented by microscopic examination.

(*2*) *Thickness of Enamel Layer:* The effect of thickness or the related property (weight per unit area) on the reflectance was studied for each enamel.

(*3*) *Difference in Optical Index between Scattering Material and Glass Matrix:* The identity of the crystalline material was determined by X-rays, and the indices of refraction of the various mineral forms were obtained from tables. Measurements on the glass matrix of various enamels in the group showed an average index of about 1.50.

(*4*) *Particle Size of Scattering Material:* The particle size was estimated from X-ray patterns and microscopic examination.

(*5*) *Distribution of Scattering Material:* The distribution was observed in thin sections made from the fired enamels.

(*6*) *Absorption Characteristics of Scattering Material and Glass Matrix:* No specific attempt was made to measure the absorption properties of an enamel, although the reflectance was measured and the absorption had some effect on it.

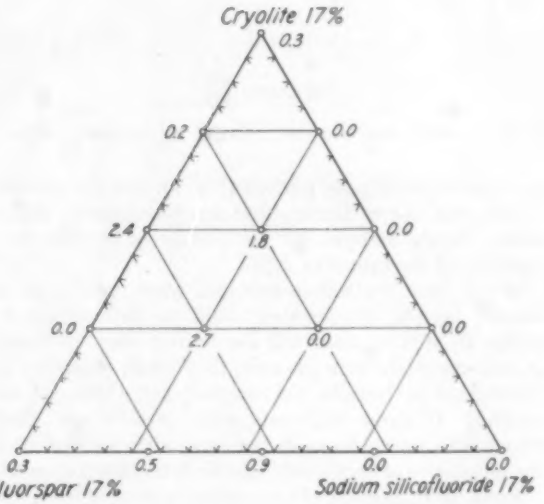

FIG. 9.—Per cent villiaumite (NaF) in fired enamel as determined by X-ray analysis; batch composition and mill additions same as in Fig. 5.

(*7*) *Wave-Length of Incident Light:* Only white light was used in the reflectance measurements.

In studying the variations in the opacity of these enamels, it was found that there were two factors

which were important, *viz.*, the identity and the quantity of the opacifying materials present. It was important, therefore, to stress the investigation of these properties. X-ray analysis has been shown by several authors to be a satisfactory means of determining the identity of the crystalline material present in fired enamels. Thus, if a method for obtaining quantitative results from an X-ray pattern could be developed, an excellent means would be available to study the two most important factors mentioned.

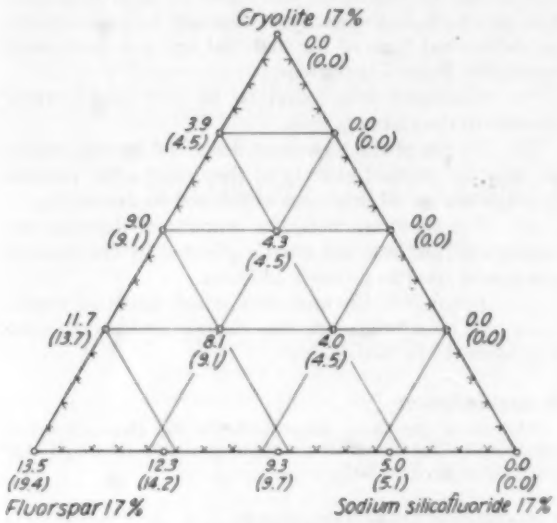

FIG. 10.—Per cent fluorite (CaF_2) in fired enamel as determined by X-ray analysis; theoretical amounts on basis of melted composition are shown in parentheses; batch composition and mill additions same as in Fig. 5.

Such a method has been developed for the analysis of crystalline mixtures. This paper demonstrates the application of this technique to the study of enamels, in which a large percentage of amorphous material is present, and the correlation of the data thus obtained with that obtained by microscopic examination to provide a clear explanation of how opacity is produced in fluoride-containing enamels.

The results of the X-ray and reflectance studies are shown in Figs. 5, 9, 10, and 11. Figure 5 shows that the lowest opacity was obtained with enamels high in fluorspar and that the effect of additions of cryolite or sodium silicofluoride was about the same. This seems hard to explain, until it is seen in Fig. 11 that these two materials produce about equal quantities of cryolite in the fired enamel. Because cryolite is the most effective opacifying material present in large amounts in the enamels, the opacity is mainly dependent on the quantity of cryolite present.

The total quantity of crystalline material present in the enamels studied was about the same in each case, *i. e.*, about 15% (see Figs. 9, 10, and 11). The differences obtained in opacity are therefore due to the efficiencies of the opacifying materials. The differences in the efficiencies of the materials are due to two main causes, *viz.*, (1) the difference in refractive index between the particles and the glass matrix and (2) the size of the particles. On the basis of index alone, cryolite, with an index of 1.34, would be expected to be a more effective opacifier than fluorite with an index of 1.43. It was also found by microscopic study that the high fluorspar enamels contained some coarse and some extremely fine crystalline material, and the enamels high in cryolite contained fine particles of fairly uniform size. Thus the cryolite particles, in addition to having a more desirable refractive index, also have a particle size which gives better opacity. The increase in opacity in enamels in which sodium silicofluoride was increased at the expense of cryolite as a raw batch addition was apparently due to a change in the structure of the enamel. In the enamels in which cryolite was used as a batch addition, the boundaries of the original grains of frit were still fairly well defined in the fired enamel. When cryolite was replaced by sodium silicofluoride, the frit-grain boundaries became much less distinct in the fired enamel, and the enamel had the appearance of having been stirred. A possible explanation of this may be that the substitution of sodium silicofluoride for cryolite gave a more fluid enamel. The bubbles retained in this enamel were somewhat smaller than those found in the enamel high in cryolite. This also suggests a more fluid enamel. The primary factors, however, controlling the opacity of these enamels were the identity and quantity of the crystalline materials present.

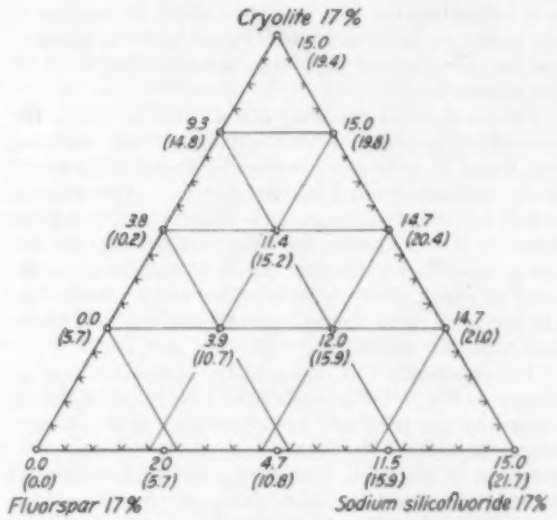

FIG. 11.—Per cent cryolite in fired enamel as determined by X-ray analysis; maximum possible theoretical amounts on basis of melted composition are shown in parentheses; batch composition and mill additions same as in Fig. 5.

Because the opacity of fluoride enamels is affected by the particle size of the fluoride compounds separating in the enamel glass and because the reflectance was determined from an enamel fired on a piece of sheet iron, all of the heat treatment the enamel received before the reflectance readings were taken had some effect

on its opacity. This heat treatment includes the time and temperature of smelting, the rate of quenching, the time and temperature of firing, and the rate at which the piece was finally cooled. In preparing these enamels, each enamel received the same heat treatment. The smelting schedule used may not have been the best for all the enamels studied, inasmuch as it was determined only for one enamel composition. For example, the enamels high in fluorspar were more refractory, so probably the enamels in this region would have been improved by smelting at a higher temperature, although in general quite satisfactory enamels were obtained. By using an automatically controlled electric resistor furnace, it was possible to give each enamel practically the same treatment during smelting.

The accuracy of the X-ray analysis is probably best shown by the curves for the standards (Figs. 6, 7, and 8). These data show that the greatest error is about $\pm 1/2$ of 1% for NaF or CaF_2 and $\pm 1\%$ for cryolite. The greatest source of error in this method of X-ray analysis is in estimating the base line from which the heights of the peaks are to be measured. Care must be taken to use the same general type of base line as that used for the standards.

The amount of fluorine, not accounted for in the crystalline material determined by X-ray analysis, was found to be nearly constant at about 2.8% for all of the enamels studied (see Table VI). This fluorine is lost by volatilization or it is dissolved in the glass. Some of it is undoubtedly volatilization loss, but because there is no definite variation according to the form in which the fluorine is added in the raw batch, the loss must occur from the fused glass, and it is therefore relatively small.

The practically flat region in the reflectance triaxial diagram (Fig. 5) for enamels Nos. 7, 8, 11, 12, and 13 is caused by the relatively low reflectance of the fluorite which separates out first. Very little cryolite separates out in this area; instead it goes into solution and provides fluorine to saturate the glass, thus permitting the calcium fluoride which crystallizes more readily to separate out.

The calculation of the fluorine unaccounted for also serves as a rough check on the accuracy of the X-ray analysis. If the analyses were correct and all of the enamels were treated the same, the unaccounted-for fluorine should either be constant or show some definite trend with variations in composition. In this investigation, all of the values were fairly constant. This conclusion agrees with that reached by Blau and Silverman,[2] who found that the fluorine loss was a constant percentage of the amount introduced irrespective of its introduction as sodium fluoride or calcium fluoride.

On the whole, the results of this investigation check well with the results of previous investigators. Cryolite, however, was found to recrystallize in a large number of these enamels as they were cooled, being formed when either cryolite or sodium silicofluoride was added in the raw batch.

[2] See reference (14) in Bibliography.

V. Conclusions

(1) The crystalline materials causing opacity in the enamels studied were cryolite, fluorite, and villiaumite.

(2) For the range of composition studied, recrystallized cryolite was found to be the most important opacifying material.

(3) The method of quantitative X-ray analysis used in this investigation was found to be satisfactory. The accuracy of the analysis depends to some extent on the crystal form of the material and the number of crystalline materials present.

(4) Fluorspar was found to be less soluble than cryolite in the enamels used.

(5) By use of the technique described herein, enamels may be studied exactly as they exist after passing through the usual processes employed in enameling.

(6) For these enamels, the amount of fluorine lost during smelting was not greatly affected by the fluoride compound used as a batch addition.

(7) Because of the ease with which smelting conditions can be reproduced, the electric resistor furnace was found to be satisfactory.

Acknowledgment

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Bibliography

(1) Lord Rayleigh, "On the Light from the Sky, Its Polarization and Color," *Phil. Mag.*, **41**, 107, 274 (1871).

(2) Lord Rayleigh, "On the Diffraction of Light by Spheres of Small Relative Index," *Proc. Roy. Soc.* [London], **90A**, 219 (1914).

(3) Gustav Mie, "Beiträge zur Optik trüber Medien, speziell Kolloidaler Metallösungen," *Ann. Physik*, **25**, 377 (1908).

(4) C. Cheneveau and R. Audubert, "Sur l'Absorption par les Milieux Troubles; Influence du Diametre et du Nombre des Particles," *Compt. Rend.*, **168**, 553, 684 (1919).

(5) J. W. Ryde and D. E. Yates, "Opal Glasses," *Jour. Soc. Glass Tech.*, **10** [39] 274–94 (1926); *Ceram. Abs.*, **6** [3] 97 (1927).

(6) J. W. Ryde, "Scattering of Light by Turbid Media: I," *Proc. Roy. Soc.* [London], **131A** [817] 451–64 (1931); J. W. Ryde and B. S. Cooper, Part II, *ibid.*, pp. 464–76 (1931); *Ceram. Abs.*, **10** [8] 554 (1931).

(7) J. W. Ryde and B. S. Cooper, "Theory and Specification of Opal-Diffusing Glasses: I," *Jour. Soc. Glass Tech.*, **16** [64] 408–30 (1932); J. W. Ryde, B. S. Cooper, and W. A. R. Stoyle, Part II, *ibid.*, pp. 430–49 (1932); *Ceram. Abs.*, **12** [7] 256 (1933).

(8) C. Dunbar, "Particle Size and Concentration in Opal-Diffusing Glasses," *Jour. Soc. Glass Tech.*, **17** [68] 411–32 (1933); *Ceram. Abs.*, **13** [5] 113 (1934).

(9) G. F. A. Stutz, "Scattering Light by Dielectrics of Small Particle Size," *Jour. Franklin Inst.*, **210** [1] 67–85 (1930); *Ceram. Abs.*, **10** [4] 306 (1931).

(10) P. Kubelka and F. Munk, "Ein Beitrag zur Optik der Farbenstriche," *Z. tech. Physik*, **12**, 593 (1931).

(11) "Reflectance Test for Opaque White Enamels," *Porcelain Enamel Inst. Bull.*, p. 7 (1936).

(12) J. F. Hyslop, "Opal Glass," *Jour. Soc. Glass Tech.*, **11** [44] 362–74 (1927); *Ceram. Abs.*, **7** [5] 283 (1928).

(13) A. Silverman, "Opacifiers of Glass," *Glass Ind.*, **11**, 53 (1930).

(14) H. H. Blau and A. Silverman, "Liberation of Fluorine in Fluoride-Glass Manufacture," *Ind. Eng. Chem.*, **26** [10] 1060–62 (1934); *Ceram. Abs.*, **14** [10] 244 (1935).

(15) A. I. Andrews, G. L. Clark, and H. W. Alexander, "Progress Report on Determination of Crystalline Compounds Causing Opacity in Enamels by X-Ray Methods," *Jour. Amer. Ceram. Soc.*, **14** [9] 634–39 (1931).

(16) A. I. Andrews, G. L. Clark, and H. W. Alexander, "Determination by X-Ray Methods of Crystalline Compounds Causing Opacity in Enamels," *ibid.*, **16** [8] 385–92 1933).

(17) A. I. Andrews and J. P. Breen, "X-Ray Investigation of the Opacifying Compounds Present in Sheet-Iron Cover Enamels," *ibid.*, **16** [7] 325–27 (1933).

(18) R. M. King, "Fluoride Investigations: I–II," *Ohio State Univ. Eng. Expt. Sta. Bull.*, No. 76 (1933).

(19) A. I. Andrews and E. E. Howe, "Effect of Fluorides on Properties of White Sheet-Iron Enamels," *Jour. Amer. Ceram. Soc.*, **17** [10] 288–91 (1934).

(20) J. D. Tetrick, "Opacity Development in Cover Enamels for Sheet Steel," *ibid.*, **18** [10] 314–18 (1935).

(21) W. Mialki, "Röntgenographische und Optische Untersuchungen über die Türbung von Emails durch Fluoridzusätze," *Sprechsaal*, **68** [41] 631–34; [42] 646–50; [43] 662–64; [44] 674–76; [45] 688–90 (1935); *Ceram. Abs.*, **15** [3] 86 (1936).

(22) G. L. Clark and D. H. Reynolds, "Quantitative Analysis of Mine Dusts; X-Ray Diffraction Method," *Ind. Eng. Chem., Anal. Ed.*, **8** [1] 36–40 (1936); *Ceram. Abs.*, **16** [11] 356 (1937).

SOLUBILITY OF COLORED GLAZES IN ORGANIC ACIDS*

By R. F. Geller and A. S. Creamer

Abstract

The purpose of this study was to determine primarily which, if any, of the glazes tested constituted a health hazard because of lead or other toxic oxides which might be dissolved from them; and, secondarily, to develop suitable test procedures for future control work.

A conference of representatives of the U. S. Potters Association, the Food and Drug Administration of the Department of Agriculture, and the National Bureau of Standards was held, and a series of accelerated and simulative service tests was outlined. These tests were made on specimens from six coöperating manufacturers.

It was shown that the lead extracted by pouring either hot, distilled vinegar (5% acetic acid) or an 0.5% solution of citric acid in a cup and leaving it to cool in contact with the glaze for ½ hr. would be as much, or more, than the lead normally extracted by jams and fruit juices. With the same or a similar test procedure, a citric-acid solution of 10% strength may be required to indicate how much lead might be taken up by lemonade or vinegar.

The results also indicate that glazes of one color only, among those tested, constitute a probable health hazard. Two other glazes from one manufacturer, however, were found to be marginal, and a third may cause trouble if indicated corrective measures, such as a preliminary acid wash, should be neglected by the manufacturer.

I. Historical

The use of lead in glazes may date back to Assyrian culture of the second millenium. It found widespread use in Persia and Turkey during the Middle Ages, and it was being used in Europe in the 12th Century. The toxic possibilities of lead, however, were not discovered because of its use in glazes but because of its application, even by ancient peoples, as a clarifier and sweetener of wine. The undesirable possibilities of this practice were discussed as early as 1616.[1] The oldest account of poisoning from "sweetened" wines is contained in a French ordinance of 1696,[2] and in 1786 Beckman[3] also records the necessity of discouraging this practice.

A reign of terror in Europe during the middle 18th Century, occasioned by lead poisoning, prompted inquisitive minds to investigate the possibility of lead being extracted by wines from glazes known to have been compounded in part from litharge. This was found to be the case,[4] but it seems that the first definite legal action on lead glazes was not taken until 1887, when a German statute[5] stipulated that glazes giving up perceptible amounts of lead to 4% acetic acid solution, during ½-hr. boiling, could not be used on food containers.

The problem was investigated at great length by Thorpe and his co-workers in England,[6] and Thomason[7] studied lead solubility in acetic, hydrochloric, and

* Scheduled for presentation at the Forty-First Annual Meeting, American Ceramic Society, Chicago, Ill., April 17, 1939 (General Session Symposium on Glaze Properties). Received February 14, 1939.

[1] M. Citois, "De novo at populari apud pictones dolore colico bilioso diatriba," Potiers (1616).

[2] M. Delamare, "Traité de la Police," Paris, **1**, 615 (1713).

[3] J. Beckman, "Beiträge z. Gesch. der Erfindung," Leipzig, **1**, 179 (1786).

[4] T. Tronchin, "De colica pictorium," Geneva (1757).

[5] Reichsgesetzblatt, 273 (1877).

[6] T. E. Thorpe, Rept. of Govt. Lab. on Question of the Employment of Lead Compounds in Pottery, London, 1901.

[7] W. Thomason, "Attempt to Ascertain Absolute Toxic Possibilities of Fritted Lead Glazes," *Trans. Ceram. Soc.* [England], **9**, 198–208 (1909–10).

lactic acids, in pepsin and in pancreatic extract.[8]

Cases of lead poisoning were reported in 1922 in Lower Austria[9] among consumers of cider fermented in plumbiferous containers, and a few years later[10] investigations in Massachusetts established the fact that water, containing as little as 0.1 part per million of Pb, produced symptoms of poisoning. Their findings showed also that, of the observed cases in which 1 mg. or less was ingested daily, 21% showed symptoms of poisoning, and 50% of those ingesting 1 to 2 mg. daily showed symptoms. These startling results appear to be significant when considered with the findings of Jackson and Jackson[11] to the effect that as little as 0.1 grain of lead per gallon of cider (equivalent to 1.7 parts per million) gave acute symptoms to the consumers. Considerable helpful information on the contamination of foods may be found in a report by Monier-Williams[12] and by Mason,[13] who states, "The writer believes that no water to be used for drinking purposes should contain lead compounds in quantity greater than what would correspond to $^1/_2$ part per million of metallic lead." This quantity at present is the maximum permissible in water supplied by public carriers in this country, and it furnishes one point of reference for limits of lead dissolved from glaze. The other point is furnished by the tolerance of 0.018 grain of lead per lb. of food (2.57 parts per million) established by the Food and Drug Administration. More recently, the U. S. Department of Agriculture raised this tolerance to 0.025 grain per lb. (equivalent to about 3.57 parts of Pb per million parts of food) based upon investigations made by the U. S. Public Health Service. There is reason to believe, however, that a tolerance for "lead" in solid foods may be too lenient for application to lead ingested in solution as the salt of an organic acid. Therefore, the tolerance of $^1/_2$ part per million in drinking water should not be lost sight of.

The present investigation was occasioned by the kaleidoscopic deluge of colored tableware and kitchenware which has met the popular fancy during the last few years. Although the greater part of these colored coatings on semivitreous articles are matured at temperatures just as high as those used for the harmless clear glazes and the clear glazes (all of which contain some lead) not infrequently are used as the vehicle for the color, it soon became evident that some color stains had a most undesirable effect on solubility. A specific case in which nausea was believed to have been caused by tea flavored with lemon juice and drunk from a green cup came to the attention of the Food and Drug Administration. The matter was referred to the National Bureau of Standards, and a conference was held on May 21, 1938, attended by representatives of the U. S. Potters Association, the Food and Drug Administration, and the National Bureau of Standards. A series of tests, to be made in coöperation with six manufacturers, was outlined, and it is the results of these tests which are reported here.

II. Purpose

The purpose of the work was essentially threefold, *viz.*, (*a*) to develop test procedures both for treatment of ware and for analysis of dissolved materials, (*b*) to correlate results of relatively rapid and standardizable laboratory tests with results of service conditions, and (*c*) to determine which of the representative glazes submitted might constitute a health hazard.

III. Materials and Methods

Bowls, fruit dishes, and cups were submitted by the six coöperating companies, and usually one dozen specimens of each shape and color were available. Four colors (tangerine, yellow, bright green, and cobalt blue) were represented by each manufacturer, but additional colors and shades were submitted by some. The maximum, from one company, was 20 colors.

A number of test methods was tried, but all were discarded except those given in Table I. These included holding on the steam bath or holding at "room temperature." Both involve temperature conditions which are difficult, if not impossible, to duplicate under ordinary conditions. The symbol accompanying each test was adopted for convenience to designate that test in the figures.

Unless otherwise designated in Table I, the lead dissolved was determined by extraction with diphenylthiocarbazone, called "the dithizone method."[14] In the case of fruit juices and jams, it was necessary to ignite and take up the residue in acid. Determination by precipitation, as the sulfide with H_2S, followed customary chemical procedure. The amount present was approximated by colorimetric comparison with standards containing $^1/_2$, 1, 2, 4, and 6 parts of Pb per million parts of solution. If more than 6 parts per million were present in the test solution, an aliquot portion was used.

Comparison standards prepared with vinegar could be used for about 2 hours at most. In this connection, both the test and the comparison solutions, prepared with acetic acid or citric acid, were unsatisfactory. The nature of the precipitate imparted a "smoky" color to the solutions and made comparisons difficult or impossible. The condition was corrected by diluting

[8] The preceding references and many others may be found in the following articles: (*a*) J. W. Mellor, "Durability of Pottery Frits, Glazes, Glasses, and Enamels in Service." *Trans. Ceram. Soc.* [England], **34,** 113–90 (1934–35); *Ceram. Abs.*, **16** [5] 154 (1937).
(*b*) J. H. Koenig, "Lead Frits and Fritted Glazes," *Ohio State Univ. Eng. Expt. Sta. Bull.*, No. 95 (July, 1937); *Ceram. Abs.*, **16** [9] 280 (1937).

[9] G. Stiefler, *Zeit. Neurol. Psych.*, **77,** 25 (1922).

[10] Wade Wright, C. O. Sappington, and Eleanor Rantoul, *Jour. Indus. Hygiene*, **10,** 234 (1928).

[11] M. C. N. Jackson and L. N. Jackson, *The Lancet*, **223,** 717 (1932).

[12] G. W. Monier-Williams, Rept. on Public Health and Medical Subjects, No. 29, Ministry of Health, London, England (1925).

[13] W. P. Mason, Examination of Water. J. Wiley & Sons, Inc., New York, N. Y.

[14] The procedure used was essentially that given in (*a*) "Method for Determining Lead in Food," *Jour. Assoc. Official Agr. Chem.*, **17,** 123 (1934) (separate copies no longer available); (*b*) "Method for Determining Lead in Canned Food," *ibid.*, **18,** 315 (1935); copies obtainable from the Association, Box 540, Benj. Franklin Sta., Washington, D. C.

these acids with a 1/4 % solution of gelatine. Resultant test liquids and standards containing up to 6 parts of Pb per million parts could be compared satisfactorily. The standards, furthermore, remained constant in color for as long as 2 days.

Copper was determined by "carbamate extraction," using sodium diethyldithiocarbamate and the procedure followed by the U. S. Bureau of Fisheries.[15] Values are believed to be significant to 0.1 part per million. The following method, giving results significant to 1 part per million, was also used. A 150-ml. portion of test solution was evaporated to dryness, ignited, evaporated with HNO_3, and treated in a porcelain crucible with 0.5 ml. NH_4OH. The shade of blue obtained was compared with standards prepared in the same way.

No test was developed for antimony because, from results for the yellow glazes, it was evident that a total of not more than 1/2 part of material per million parts of reagent was dissolved by the severest tests.

Blank determinations for lead and copper showed that the white vinegar used in the tests (Table I) contained 0.3 and 1.0 part per million, respectively, and that the brown vinegar contained not more than 0.1 part of lead per million parts of vinegar.

TABLE I

TEST METHODS

Methods 1, 2, 10, 14, 15, and 16 are primarily for laboratory work; methods 3 to 9, inclusive, and 11 to 13 inclusive, were designed to simulate conditions in service (*i.e.*, home or restaurant use).

No.	Symbol	Method
1	*WV* 1/2 hr. H_2S	Cup or fruit dish, into which 150 ml. boiling white vinegar (about 5% acetic acid) had been poured, covered with 3-liter beaker for protection from drafts; after standing 1/2 hr., vinegar removed to Pyrex-brand flask and subjected to H_2S test for Pb.*
2	*WV* 1/2 hr.	Same as test No. 1, except lead determined by dithizone method.†
3	*PJ* 70° 2 days	Cup containing 150 ml. unsweetened pineapple juice kept 2 days in room maintained at 70° F.
4	*GFJ* 70 2 days	Same as test No. 3, except unsweetened grapefruit juice used.
5	1/2 *CAc* 70° 2 days	Same as test No. 3, except 0.5% citric acid used to simulate lemonade.
6	*BV* 70° 2 days	Same as test No. 3, except brown vinegar (4.4% acidity) used.
7	*WV* 70° 2 days	Same as test No. 3, except distilled vinegar (5% acidity) used.
8	*WV* 40° 2 days	Same as test No. 7, except specimens held 2 days in refrigerator at 40°F.
9	*WV* RT‡ 2 days	Same as test No. 7, except specimens held at RT (85 ±5°F).
10	*WV* 122° 1 day	Same as test No. 7, except specimens held 1 day at 122°F (50°C) and lead determined by H_2S precipitation.
11	*CJm* RT 60 days	Specimens containing cherry jam held at RT (80 ±10°F) 60 days (2 months).
12	*SJm* RT 7 days	Specimens containing strawberry jam held at RT (80 ±10°F) 7 days.
13	*SJm* RT 60 days	Same as test No. 11, except strawberry jam used.
14	1/2 *CAc* 1/2 hr.	Same as test No. 1, except solution containing 1/2% citric acid and 1/4% gelatine used.
15	*CAc* 1/2 hr.	Same as test No. 14, except solution contained 1% citric acid.
16	10 *CAc* 1/2 hr.	Same as test No. 2, except solution contained 10% citric acid.

* This test may give too high values for "lead" because other metals, such as copper, which may be present also, are precipitated; the test was suggested to the industry for control and development work shortly after the conference held in May, 1938; it became known as the National Bureau of Standards Tentative Test, *Nat. Bur. Stand. Tech. News Bull.*, No. 255 (July, 1938).

† The dithizone extraction, followed by electrolysis, is a specific test for lead, except in the presence of bismuth; the dithizone method was used in all of the tests except Nos. 1, 10, 14, and 15.

‡ RT = room temperature.

[15] E. J. Coulson, *Jour. Assoc. Official Agr. Chem.*, 20, 178 (1937).

IV. Results and Conclusions

The results are presented in Figs. 1 to 8, inclusive, and some of the values are plotted in several graphs to facilitate comparison and correlation with the various factors involved. Each plot, unless otherwise stated, represents the average of at least two determinations.

Data obtained with test No. 1 on cups in various colors from the six coöperating manufacturers are presented in Fig. 1 (*left*). Values for some intermediate shades of yellow, brown, blue, and gray (or "white") are omitted, but in no case did they exceed 1/2 part per million. Except for the maroon glaze of one manufacturer, the only specimens to give up more than 2 parts per million of Pb were the tangerines (reds) and the greens.

Some of the dark blues and yellows showed solubilities equal to, or in excess of, 1 part per million. These colors, together with the maroon mentioned and a brown, were subjected to tests Nos. 3, 4 5, 6, and 7. The results are shown in Fig. 1 (*right*), and values from test No. 1 are repeated for comparison.

The combined data of Fig. 1 show that (*a*) glazes of high resistance to solution under the conditions of test No. 1 (not over 1 part per million of Pb) will also present little, if any, hazard to health even if "lemonade" (test No. 5) or distilled vinegar (test No. 7) is left in contact with them for as long as 2 days; (*b*) with some colors (*e.g.*, dark blue and maroon), contact with vinegar, or citric acid solution of lemonade strength, for 2 days may be dangerously more severe than the tentative test (No. 1) indicates; and (*c*) the limited time available for this investigation should be concentrated on the tangerine and green glazes.

The specimens of tangerine and green from two plants accordingly were subjected to a series of tests (Fig. 2).

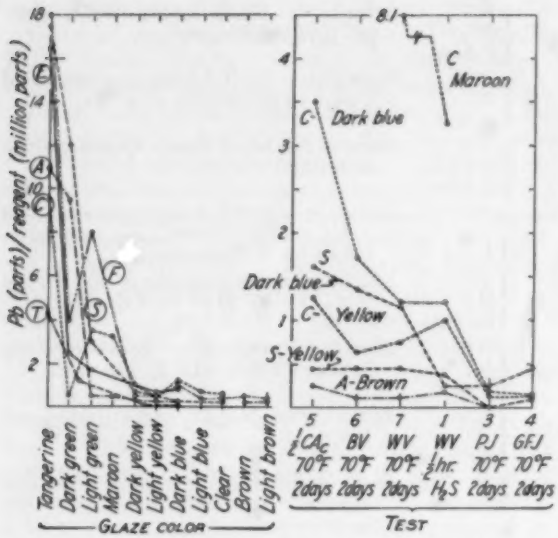

FIG. 1.—(*Left*) effect of test No. 1 (see Table I) on glazes in 11 colors from 6 manufacturers; (*right*) effect of tests Nos. 3 to 7, inclusive, on glazes of relatively low solubility according to test No. 1; in this figure, as in the others, the letters *A*, *C*, *E*, *F*, *S*, and *T* refer to the manufacturers of the ware tested.

The first 5 tests (reading from left to right) show that home use with fruit juices and jams would be less severe than laboratory test No. 2,* while tests Nos. 6, 5, 7, and 9 (representing home use with lemonade and with vinegar) would be more severe, and the glazes, under these conditions, might be unsafe; *e.g.*, a vinegar containing 25 parts of lead per million would have little

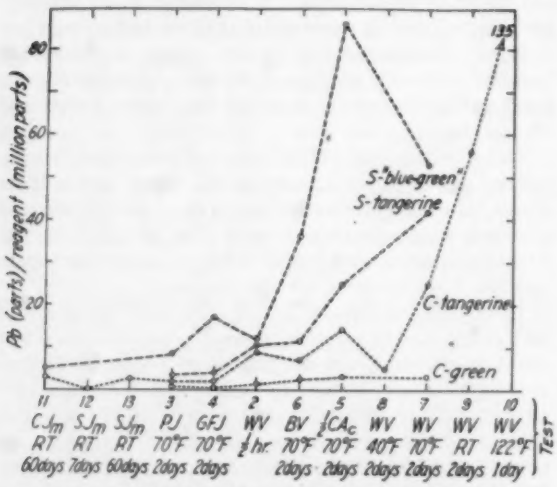

FIG. 2.—Effect of accelerated test (No. 2) and simulated service tests (Nos. 3 to 13, inclusive) on tangerine and green glazes from 2 manufacturers. All determinations by dithizone extraction; *RT* (room temperature, about 85°F).

* Test No. 2 results were plotted here, instead of test No. 1, to make the method of analysis common for all tests.

more than 1 mg. of lead in $1^1/_2$ fluid ounces (and $1^1/_2$ oz. is only about "2 fingers"). Correspondingly, an 8-oz. tumbler of lemonade would have 6 mg. of lead, and, in the references cited, it was stated that ingesting 1 mg. daily produced symptoms.

Tests Nos. 8, 7, 9, and 10 were made to show the effect of variation in temperature, *viz.*, that vinegar may take up only 5 parts per million during 2 days in a refrigerator, 25 parts in a room when the climate is moderate, and more than 50 parts in summer heat. Test No. 10 indicates what might be expected if such glazes were used, *e.g.*, in warming ovens.

Based on the results described, tests Nos. 1, 2, 5, 7, and 16 were selected as representative of both laboratory and service tests. Five tangerine and six green glazes, subjected to these treatments, are represented in Fig. 3. Plotted in the general order of relative severity, the values show first that this order is not the same for the 2 colors but that more lead is dissolved from green glazes by "lemonade" than by white vinegar under the same conditions. Figure 3 shows also, in the large majority of cases and test for test, that the green glazes are more reluctant to give up lead than the tangerines. The indication of Fig. 2 that the tentative test (Nos. 1 or 2) may not be nearly as severe as "home conditions" (Nos. 5 and 7) is substantiated. The substitution of $^1/_2$% citric acid solution for distilled 5% acetic acid vinegar in tests Nos. 1 and 2 also produces roughly comparable results with the tangerine glaze.†

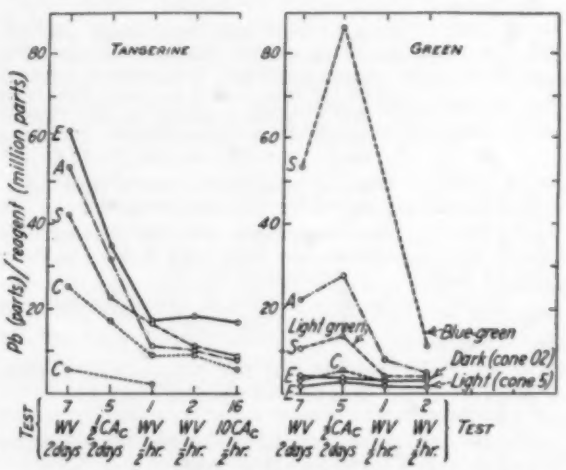

FIG. 3.—Effect of accelerated tests (Nos. 1, 2, and 16) and service tests (Nos. 5 and 7); (*left*) on tangerine glazes and (*right*) on green glazes from 4 manufacturers.

Two additional points of interest are brought out by the data in Fig. 3 (*right*), *viz.*, (*a*) the effect of the stain on the solubility of a base glaze and (*b*) the effect of the glost temperature. The first, (*a*), is illustrated by the graphs for a "blue-green" and a "light green" glaze.

† Citric acid solutions are more desirable than vinegar or acetic acid solutions for laboratory work because solutions of known strength can be prepared and maintained more conveniently.

The only known difference between these glazes is that the latter contains $^1/_2$ the identical stain used in the former. The clear or "base glaze" to which the stain had been added gave up only 0.6 part per million of lead in test No. 5. The second point, (*b*), is illustrated by the plots, identified as "dark cone 02" and "light cone 5." Naturally, the compositions of the two base glazes (and also probably those of the stains) differed, but the results show that glazing at the lower temperature need not materially lower the resistance to solution.

The possibility of substituting citric acid solution for vinegar was investigated further (see Fig. 4). Because of the shortage of cups, test results given in the larger graph were obtained with fruit saucers; they show that differences obtained with tests Nos. 1 and 14 are not significant.

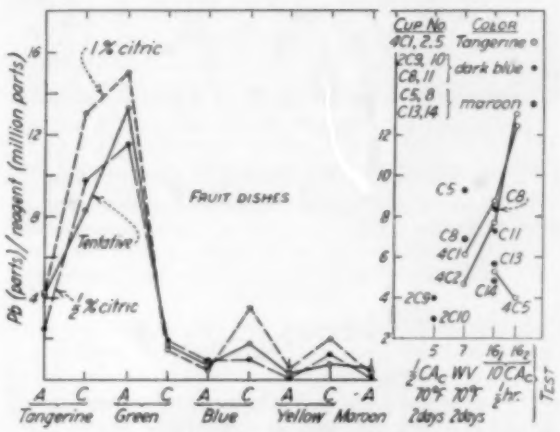

FIG. 4.—(*Left*) fruit dishes: "tentative," test No. 1; $^1/_2$% citric, test No. 14; 1% citric, test No. 15; relative results with tests Nos. 1, 14, and 15 on 9 glazes in 5 colors. (*Right*) cups: relative results with 10% citric acid solution, test No. 16; and simulated service tests Nos. 5 and 7. Test No. 16 was made twice on cups 4C1 and 4C2, after test on No. 7 and twice on cup 4C5 previously untested.

Test No. 16 was made on tangerine, maroon, and blue cups from one manufacturer to determine the strength of citric acid required in an accelerated test to dissolve glaze comparable to vinegar or lemonade in contact with the glaze for 2 days at 70°F (test No. 7). The data are plotted in Fig. 4 (*right*); graphs 4C1, 4C2, and 4C5 are for 3 tangerine cups from the fourth shipment. Cups 4C1 and 4C2 were subjected to test No. 7 and then twice to test No. 16; cup 4C5 was subjected twice to test No. 16. The indication is that a solution containing at least 10% citric acid (when substituted for vinegar in the tentative method), in order to obtain values comparable with those of tests Nos. 5 or 7, will give higher values for some colors (*e.g.*, dark blue) and lower values for others (*e.g.*, maroon).

The values for individual cups given in Fig. 4 (*right*) led to the question as to what variations were found among supposedly duplicate cups. Typical examples are given in Table II. Results with tangerine cups were especially erratic. One of the factors which may be responsible is difference in heat treatment. It was thought this could be illustrated by testing the glaze on the inside and outside of several cups. The graphs in Fig. 5 (*left*) show that a significant difference is to be found on the same cup; differences between cups therefore are not surprising.

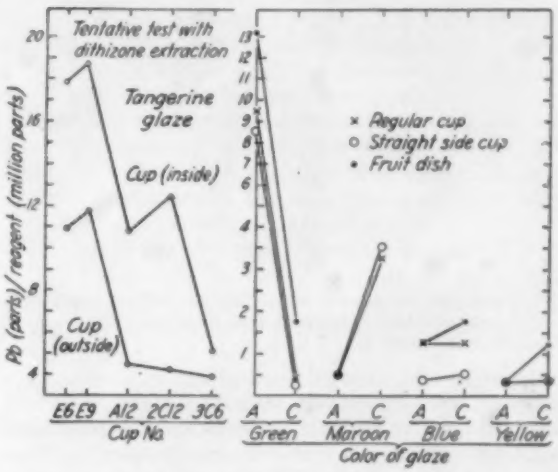

FIG. 5.—(*Left*) relative solubility on inside and outside of 5 cups from 3 manufacturers; (*right*) effect of shape of specimen (and consequent variation in surface exposed to the 150 ml. of reagent) on results with "tentative" test (test No. 1).

Another factor to be considered in testing commercial ware with a specified amount of reagent (in this case, 150 ml. per cup) is the variable surface exposed because of differences in design. Some glazes were represented by (*a*) the "regular" (or approximately hemispherical) cup, (*b*) a straight-sided cup in the shape of an inverted and truncated cone (frustum), and (*c*) fruit dishes. The tentative test (No. 1) was conducted on each, using 150 ml. of vinegar for each shape. The results (Fig. 5, *right*) show that the greater surface exposed by this dish will usually give slightly higher values for Pb dissolved, but the differences introduced by the shapes tested have little significance in the tentative test.

In addition, 3 bowls in green glaze were subjected to tests Nos. 1, 5, and 7, using 325 ml. of reagent because the capacity of the bowls was in the ratio of 325 to 150 to the capacity of comparable cups. The results for cups and for bowls, respectively, were as follows: test No. 1, 7 and 8 parts of lead per million; test No. 5, 26.0 and 29.1 parts per million; test No. 7, 24.5 and 19.0 parts per million. This shows that similar shapes in various sizes will give comparable results, if proportionate amounts of reagent are used.

An appreciable difference had been found in the amount of lead indicated by H_2S precipitation and by dithizone extraction for some green and also some tangerine glazes. The precipitation of tin might account for the difference in the case of the tangerine glaze. The difference, however, was found with a

TABLE II

VARIATIONS AMONG DIFFERENT SPECIMENS OF SAME GLAZE

Manufacturer	Test No.	Tangerine cup*		Yellow cup*		Green cup*		Blue cup*	
C	1	C13	12	C6	1	C1	1/2	C6	1.5
"	"	3C1†	12	C7	1	C2	<1/2	C7	1.0
"	"	3C3	9	2C11	1	2C11	>3	2C12	1.0
"	"	3C6	6	2C12	1	2C12	3		
"	2	2C11	11.1						
"	"	2C12	12.4						
"	"	3C5	5.9						
"	"	3C6	5.1						
"	5	2C7	13.8	2C9	0.5	2C9	5.9	2C9	4.0
"	"	2C8	20.0	2C10	1.0	2C10	5.6	2C10	3.0
A	1	A1	11	A4	<1/2	A4	10	A4	1.0
"	"	A4	9	A5	<1/2	A5	9	A5	0.5
"	"	A11	12			A13	>7		
"	2	A11	11.6			A6	6.0		
"	"	A12	10.0			A8	6.9		
S	7	S3	44.5	S2	0.5	S2	48.0	S2	1.2
"	"	S4	40.2	S3	0.4	S3	58.0	S11	1.1

* Values are in parts of lead (Pb) per million parts of reagent.

† Number before letter indicates shipment; thus, 3C1 in this column means tangerine cup No. 1 of the third shipment from manufacturer C.

glaze reported to contain only Pb, Al_2O_3, SiO_2, and UO_3 and uranium sulfide is not precipitated in weak acid solutions according to textbooks on the subject. This was checked by passing H_2S through vinegar containing a known amount of uranium. A slight discoloration was produced, much less than that required to account for the differences actually found. Inasmuch as there is no reason to believe that the slight amounts of uranium which might be ingested would be toxic, the matter was not investigated further.

The case of nausea (p. 134) which followed the drinking of tea from a new, green-colored cup may have been caused by copper. It was readily demonstrated that the differences in results for tests Nos. 1 and 2 could be explained by the precipitation of CuS. The data are given in Fig. 6 and were obtained for 4 cups and 4 fruit dishes on each of which test No. 1 was conducted three times; *i.e.*, the acid treatment of test No. 1 was used, and analytical methods of tests Nos. 1 and 2 were made on aliquot portions of the same liquid.

It is evident (Fig. 6) that the solubility of the green glaze on the fruit dishes, insofar as extraction of lead and copper is concerned, had been decreased materially by the first acid treatment. This interesting and important phenomenon was investigated further, and the results are plotted in Fig. 7. Cups glazed in tangerine (from four manufacturers) were subjected 4 times to test No. 1, and duplicate sets were washed with hot water and soap between each test to remove any film of colloidal silica which might have formed. In three cases, the dithizone extraction was also made (after this fourth test) on an aliquot portion of the same solution. The washing had no marked effect on the solubility. The graphs (Fig. 7, *left*) also indicate that the susceptibility of the tangerine glazes to acid attack will increase with continued use but that this increase (by the H_2S test) may not mean necessarily a proportionate increase in the lead taken up by the acid (dithizone extraction). As mentioned previously (p. 137), the difference in the amount of dissolved lead, as determined by these two methods, has not been accounted for.

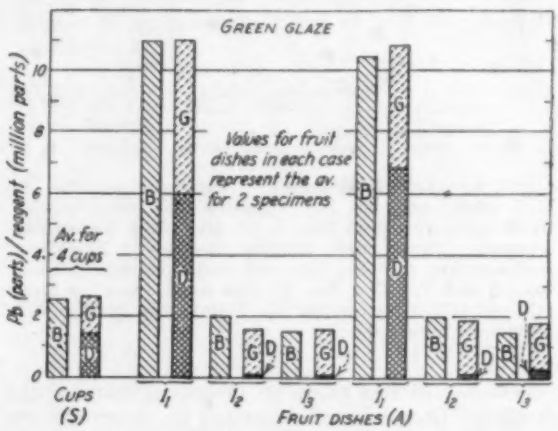
GREEN GLAZE
Pb (parts)/reagent (million parts)
Values for fruit dishes in each case represent the av. for 2 specimens
Av. for 4 cups
CUPS (S)
FRUIT DISHES (A)

FIG. 6.—Amounts of copper and lead making up the "lead" dissolved during test No. 1 as indicated by H_2S precipitation; the test was made on previously untested cups and was repeated twice on the fruit dishes. (*B*) is "lead" determined by H_2S precipitation (test No. 1); (*G*) is Cu extracted with $(C_2H_5)_2NCSSNa$; (*D*) is Pb extracted with $(C_6H_5)_2N_2CS(NH)_2$.

Figure 7 (*right*) shows the results of 4 successive tests by method No. 1 on green glazes from two manufacturers, and again with and without intermediate washing. The first acid treatment has reduced the amount of lead extracted to not more than 2 parts per million, supporting the results given in Fig. 6. It will be recalled that test No. 1 is a comparatively mild treatment compared with tests Nos. 5 and 7. These two tests therefore were repeated on 2 cups. For test No. 5, the lead extracted dropped from 26.0 to 6.5 parts per million; and for test No. 7, from 24.5 to 5.9

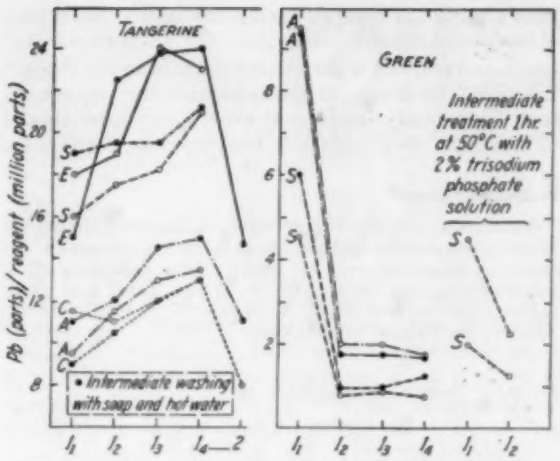
TANGERINE
GREEN
Pb (parts)/reagent (million parts)
Intermediate treatment 1 hr. at 50°C with 2% trisodium phosphate solution
• Intermediate washing with soap and hot water
1 2 3 4—2
1 2 3 4 1 2

FIG. 7.—Repeat tests: results obtained by repeating test No. 1 on tangerine cups from 4 manufacturers (*left*), and on green cups from 2 manufacturers (*right*). One series of cups was permitted to dry in air between tests; a duplicate series was washed with soap and hot water. The dithizone extraction for Pb (test No. 2) and the H_2S precipitation was also made on the same solution from the fourth test for 3 samples. The intermediate treatment with trisodium phosphate was made to simulate cleansing in a washing machine, and the upper and lower pairs of values are on cups of slightly different color from manufacturer S, and from a separate shipment.

parts per million. It was suggested furthermore that a treatment in an alkaline bath, such as ware is subjected to in commercial washing machines, might break down the glaze sufficiently to counteract the effect of the acid wash. Repeat tests were made on cups with an intermediate treatment in 2% trisodium phosphate solution at 50°C for 1 hr. The results (Fig. 7, *right*) show that the alkali had little, if any, effect.

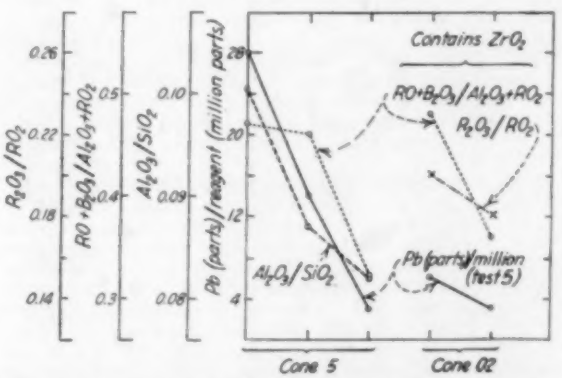

FIG. 8.—Some relations between base-glaze composition and solubility using green glazes and test No. 5.

Attempts to correlate base-glaze compositions and relative solubilities were practically without results. This is due, in large measure, to the influence of the stains on the solubilities. Some relations of possible interest are plotted in Fig. 8.

V. Discussion

This discussion deals primarily with the extent to which the results obtained have met the purpose of the work (Section II, p. 134).

The "tentative test" (No. 1, Table I) appears to be satisfactory as to the possibility of duplication in different laboratories, illustrated by the following cases:

Case 1: A sample of cups tested at the National Bureau of Standards lost 3+, 3−, 2.5, and 2.5 parts of Pb per million parts of reagent, respectively. Cups in a duplicate sample submitted to another laboratory were reported to lose between 2.5 to 3 parts.

Case 2: Average values obtained at the Bureau for four glazes from one manufacturer were tangerine 4+, green 1+, yellow <0.5, and blue <0.5; values obtained by the manufacturer in the plant laboratory were >3, >1, <0.8, and <0.8, respectively.

That determinations on individual specimens of a sample differ may reasonably be explained by actual differences in the glazes shown by data in Fig. 5 (*left*) and by similar differences obtained with the other test methods.

Correlation of results obtained with laboratory tests (Nos. 1, 2, 14, and 15) and those designed to represent conditions in home use (Nos. 3 to 13, inclusive) show that the former group of tests adequately determines the lead which might be taken up by fruit juices and jams. They do not, however, give a satisfactory measure of the lead which might be found in weak acid solutions, such as vinegar or lemonade, after 2 days of contact at ordinary temperatures (tests Nos. 5 and 7); test No. 16 was more severe for some colors and less so for others.

The proposed "solubility limit" in the tentative test of not more than 2 parts of Pb per million parts of reagent should be considered to be purely arbitrary until a decision on the matter is made by the proper state or federal agencies. It is also believed to be desirable to substitute a solution containing $^1/_2$% of citric acid and $^1/_4$% of gelatine for the white, distilled vinegar (nominally 5% acetic acid) at present specified for the tentative test.

The H_2S test for lead and the ammonia test for copper are believed to give values accurate within $\pm^1/_2$ part per million for solutions containing not more than 6 parts. The H_2S will precipitate also in weakly acidic solutions any copper, antimony, or tin which may be present, and this fact of course must be taken into consideration when the results are evaluated. Figure 6 shows, *e.g.*, that the precipitate obtained after the second and third treatments of a typical green glaze was almost entirely copper sulfide.

Whether one glaze will constitute a health hazard and another will not is still a moot question. Nevertheless, the typical glazes covered in this investigation, with one and possibly three exceptions, very probably will not offer such a hazard, provided the manufacturer exercises a modicum of care in their preparation. The first exception is the tangerine glaze from which organic acids extract quantities of lead detrimental to health as judged by the best available medical records. This condition, furthermore, does not improve

with continued use and may actually be aggravated. The two possible exceptions are the dark blue and the maroon for which values are shown in Fig. 1. Whether or not these glazes will improve with repeated use was not determined.

Although a green glaze precipitated this study, it is not considered to have a dangerous future. There is reason to believe that the lead and copper dissolved by weak acids from many green glazes as they come from the kiln are a health hazard. Fortunately, however, this high solubility appears to be a surface condition. The results in Fig. 6 (which incidentally were obtained with the least resistant of the green glazes "in production") show that a preliminary acid wash will reduce the lead absorbed during test No. 1 to a few tenths of one part per million and probably not to more than 6 parts per million during the severe conditions of tests Nos. 5 and 7. This does not seem to warrant much concern, but it would be preferable to use copper-free stains for the green glazes because they do constitute a potential danger, and every precaution should be exercised to assure their harmlessness to the user.

Acknowledgment

The authors acknowledge the assistance of the U. S. Potters Association and the six coöperating companies for material furnished and for information regarding their manufacture, and to Dr. W. B. White, Food and Drug Administration, and Dr. R. R. Sayers, U. S. Public Health Service, for helpful suggestions.

National Bureau of Standards
Washington, D. C

CERAMIC ABSTRACTS

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April, 1939
18—4

Abrasives

Abrasive finishing of stainless steel. James Lindsay. *Products Finishing*, **3** [4] 16–18 (1939).—The procedure to be followed for best results is explained in simple terms. Wheel and belt speeds are important, and they should be checked carefully from time to time. Polishing speeds of 6000 to 8000 surface ft./min. should be maintained where a satin or mat finish is desired. A buffing speed of about 8500 to 12,000 surface ft./min. is recommended for obtaining a bright finish. Where vitrified wheels are used, wheel speeds should not exceed 6000 surface ft./min. When machines exceeding this speed are used, they must be equipped with a resinoid or rubber-bonded wheel. These wheels will operate successfully at 9000 surface ft./min. The proper types of cloth for use with belt polishing are listed. H.K.R.

Abrasives in grinding machines. Anon. *Times Trade & Eng.*, **44** [899] 22 (1939).—The main function of abrasive wheels is to finish machine parts which are too hard for other treatment and to give a high degree of accuracy. Abrasive wheels are useful where rapid removal of metal is required. A.B.S.

Analysis of synthetic corundum and natural corundum. A. I. Miklashevskiĭ. *Zavodskaya Lab.*, **6**, 1209–13 (1937).—Finely ground material (0.4 to 0.5 g.) is fused in a platinum crucible with potassium pyrosulfate or, preferably, with soda (2 parts) and borax (1 part). After the fusion is dissolved in water slightly acidified with H_2SO_4, it is introduced in a 250 ml. bottle. The solution must be clear. To determine silica, 40 to 50 ml. of water (in the case of 2% SiO_2, about 20 ml.) are added to an aliquot part of the solution; the mixture is neutralized by a concentrated soda (or NaOH) solution until the appearance of turbidity. $R(OH)_3$ is dissolved in 5 ml. of 2 N H_2SO_4, the solution is shaken to remove the greater part of the CO_2 (if soda was used), and 5 ml. of a 5% ammonium molybdate solution are added; the solution is diluted to 100 ml. The yellow-green solution is colorimetrically compared with a standard solution of picric acid. Sesquioxides are determined in an aliquot part of the solution (150 to 200 ml.) by precipitating them twice with ammonia. The residue is dissolved in a small amount of H_2SO_4, and the determination is fulfilled colorimetrically. The filtrate is used for CaO and MgO determinations. Alumina is determined by the 8-hydroxyquinoline method. P.B. & E.S.

Definitions of terms describing abrasive operations. H. J. Wills. *Metal Ind.* [N. Y.], **37** [1] 31–33 (1939).—W. points out the need for a standardization of terms describing abrasive operations. Seventeen operations performed by abrasive wheels are defined and described. Nine photographs. H.K.R.

Development of the American sandpaper industry. Anon. *Chem.-Ztg.*, **62** [62] 554–55 (1938).—The American sandpaper industry is reviewed in respect to control of materials and processes. The selection of cloth, paper, abrasives, and glue, microscopical testing of materials, and fabrication processes are considered. D.A.B.

Huge grinder handles work up to 40 ft. long. Anon. *Can. Machinery*, **50** [1] 24, 26 (1939).—The longest grinder of its type is capable of producing shafts 36 in. in diameter and 40 ft. long. A shaft 4 in. in diameter and 33 ft. long was ground straight within 0.0008 in. and round within 0.0002 in. The grinder is 8 ft. wide and 80 ft. long. It is driven by eight electric motor components. The grinder was produced by Norton Co. Illustrated. D.A.B.

BOOK

Grinding Wheels and Their Uses. Johnson Heywood. Penton Publishing Co., Cleveland, 1938. 367 pp. Price $3. Reviewed in *Mill & Factory*, **23** [6] 85–86 (1938).—H. gives information on modern grinding practices for shop executives, operators, etc. Practical and theoretical knowledge and descriptions of grinding practices and methods are presented. See *Ceram. Abs.*, **17** [1] 1 (1938). D.A.B.

PATENTS

Abrading tool. N. H. Knowlton (United Shoe Machinery Corp.). U. S. 2,146,302, Feb. 7, 1939 (July 21, 1937). H. R. Moulton and F. D. Kinney (American Optical Co.). U. S. 2,145,888, Feb. 7, 1939 (June 6, 1936).

Abrasive articles. E. I. du Pont de Nemours & Co., Inc. Fr. 825,538, March 4, 1938; *Chem. Abs.*, **32**, 6825 (1938).—Polyvinyl alcohol and its derivatives still soluble

in water, particularly in the form of aqueous solutions, are used to bind abrasive material to the flexible supports. Plastifiers such as glycerol or pentaglycol may be added. The binder is hardened by heat or hardening agents.

Apparatus for:

Dressing grinding wheels used for grinding or finishing gear teeth. W. C. FAIRWEATHER (B. G. Bougie). Brit. 498,356, Jan. 18, 1939 (Jan. 10, 1938).

Grinding curved blades. H. W. BARNARD. U. S. 2,147,079, Feb. 14, 1939 (Jan. 29, 1938).

Grinding spiral-shaped, conical parts with center boring. HEINRICH SCHICHT (W. Ferd. Klingelnberg Söhne). Ger. 667,151, Oct. 13, 1938 (Nov. 16, 1936); XII/67*a*. 1. D.A.B.

Honing. H. L. BLOOD (Heald Machine Co.). U. S. 2,146,414, Feb. 7, 1939 (Sept. 15, 1936).

Preventing explosions from grinding dusts or shavings which are readily combustible. WALTHER MEISSNER AND MAX GREINER. Ger. 664,466, Aug. 11, 1938 (May 26, 1936); XII/67*a*. 28.—A plate of high heat conductance, such as copper, is arranged as a quenching plate in a dust collector or shaving-collecting device over the working or grinding surface in the path of the moving dust or shavings. D.A.B.

Bit-sharpening attachment for grinding machines. W. S. SCHICK. U. S. 2,146,355, Feb. 7, 1939 (March 11, 1937).

Buffing machine. J. N. WHITEHOUSE. U. S. 2,145,961, Feb. 7, 1939 (Sept. 30, 1937).

Coating interior surfaces of hollow articles. E. C. HALL (Western Electric Co., Inc.). U. S. 2,146,819, Feb. 14, 1939 (April 23, 1937). A method of applying an abrasive coating to the interior surfaces of wire splicing sleeves.

Composite grinding wheel and method of making. NORTON GRINDING WHEEL CO., LTD. Brit. 498,951, Feb. 1, 1939 (Jan. 12, 1937).

Device for sharpening knives, etc. W. GOODENOUGH. Brit. 498,728, Jan. 25, 1939 (April 6, 1938).

Dressing fixture for grinding wheels. H. A. DANNECKER. U. S. 2,146,466, Feb. 7, 1939 (July 6, 1938).

Flexible abrasive disk. FRANK MITSCHANG, JOSEPH MITSCHANG, AND J. C. WANDER (Curtiss-Wright Corp.). U. S. 2,146,548, Feb. 7, 1939 (Feb. 19, 1937).

Forming or shaping grinding or abrasive wheels. S. A. HORSTMANN AND HORSTMAN, LTD. Brit. 497,921, Jan. 11, 1939 (July 6, 1937); divided out of 492,591, Oct. 5, 1938.

Grinder for knives and shears. W. GEVEKE. Ger. 664,107, Aug. 4, 1938 (March 18, 1936); XII/67*a*. 6. D.A.B.

Grinding apparatus for conical borings. MASCHINENFABRIK AUGSBURG-NÜRNBERG A.-G. Ger. 665,303, Sept. 1, 1938 (Oct. 23, 1935); XII/67*a*. 9. D.A.B.

Grinding machine for steels: hard-metal cutting. VOMAG-BETRIEBS-A.-G. Ger. 664,249, Aug. 4, 1938 (April 6, 1934); XII/67*a*. 5. D.A.B.

Grinding-machine work-clamping mechanism. NORTON CO. Brit. 499,349, Feb. 1, 1939 (Dec. 24, 1936).

Grinding or surface lapping machine. H. HAHN AND H. SAUTER (trading as Hahn & Kolb). Brit. 497,962, Jan. 11, 1939 (July 1, 1936).

Grinding tool for finishing inside of cylinders. PAUL FORKARDT KOMM.-GES. Ger. 665,717, Sept. 15, 1938 (June 11, 1935); XII/67*a*. 9. D.A.B.

Honing machines. A. F. BURGESS (Barnes Drill Co.). Brit. 499,637, Feb. 8, 1939 (April 27, 1938).

Lap. ALBERT SCHULTZ (Boyar-Schultz Corp.). U. S. 2,146,195, Feb. 7, 1939 (Jan. 17, 1938).

Machine for grinding razor blades. LEO STEINER. Ger. 664,721, Aug. 18, 1938 (May 2, 1936); XII/67*a*. 7. D.A.B.

Machine for grinding tubes. H. H. MINER (Landis Tool Co.). U. S. 2,147,453, Feb. 14, 1939 (Aug. 6, 1936).

Machine for precision grinding. HAHN & KOLB. Ger. 664,667, Aug. 18, 1938 (June 8, 1936); XII/67*c*. 24.01. D.A.B.

Machine for smoothing cooking utensils. JEAN AUBECQ. Ger. 664,415, Aug. 11, 1938 (Jan. 2, 1936); XII/67*a*. 31.10. D.A.B.

Making a composite abrasive wheel and mold therefor. NORTON GRINDING WHEEL CO., LTD. Brit. 498,950, Feb. 1, 1939 (Jan. 12, 1937).

Manufacture of grinding or abrading wheels. J. DOL APPLICATIONS STACO & CIE. Brit. 499,094, Feb. 1, 1939 (May 5, 1937).

Means for mounting the cutting or grinding ribs or teeth in mills of any type. OLAF KRISTOFFERSEN. U. S. 2,147,167, Feb. 14, 1939 (Jan. 7, 1937).

Method and apparatus for grinding and abrading. NORTON CO. Brit. 498,695, Jan. 25, 1939 (Aug. 1, 1936).

Process and apparatus for the manufacture of abrasive coatings. C. W. BRYAN. Brit. 498,833, Jan. 25, 1939 (July 13, 1937).

Producing ceramic-bonded abrasive wheels. ALEXANDER GUILLEAUME. Ger. 665,900, Sept. 15, 1938 (Sept. 22, 1936); VI/80*b*. 11. Ceramic-bonded abrasive wheels are made from concentric rings with binding agents of different melting points. The binding agent used for the part of the wheel lying around the hole has a higher melting point than that used for the outer part of the wheel. D.A.B.

Roll for grinding and polishing. H. R. HERCHENRIDER (Minnesota Mining & Mfg. Co.). U. S. 2,145,418, Jan. 31, 1939 (Oct. 30, 1937).

Rotary buffing device. G. R. CHURCHILL. U. S. 2,146,284, Feb. 7, 1939 (March 19, 1937).

Sandpaper drum. O. E. HADWIGER AND H. O. SCHMIDT. U. S. 2,145,980, Feb. 7, 1939 (March 4, 1938).

Tool for precision grinding of grooves with equal or unequal shaped pitch in borings. MASCHINENFABRIK AUGSBURG-NÜRNBERG A.-G. Ger. 666,026, Sept. 22, 1938 (Dec. 18, 1935); XII/67*a*. 31.03. D.A.B.

Tool for resharpening the blades of mowers, binding machines, etc. A. BRUNET. Brit. 498,445, Jan. 18, 1939 (Feb. 26, 1937).

Treatment of articles by abrasive. A. GUTMANN AKT.-GES. FÜR MASCHINENBAU. Brit. 498,601, Jan. 25, 1939 (Sept. 8, 1936).

Art and Archeology

American archeologists in ancient Athens. T. LESLIE SHEAR. *Sci. Amer.*, **160**, 90–92 (1939).—The greater part of the ancient market place has been uncovered, and many of the public buildings have been identified. This site has been occupied since about 3000 B.C. The utmost care was needed in the excavation of the numerous superimposed strata. A total of 38,000 objects and 5500 inscriptions was found and catalogued. Early graves yielded a variety of pottery vases. Old wells contained quantities of vases of different kinds, some dropped in carelessly, and pieces of sculpture of the Greek and Roman periods. W.D.F.

American pottery at New York World's Fair. ANON. *Bull. Amer. Ceram. Soc.*, **18** [2] 75 (1939).

Beautiful ceramic ware. First national ceramic contest at Faenza, Italy. GAETANO BALLARDINI. *Ceram. & Laterizi*, **1938**, May–Aug., pp. 32–37.—The principles underlying ceramic art which were agreed upon by the jury are as follows: (1) Ceramic ware and its decoration must be simple, sincere, and intelligently stylized, perceived, and realized in the Italian manner. (2) Applied art should have a utilitarian aim. (3) Ceramic plastic art is limited; the work must have its expression in terms of its material, ceramics. (4) The object of ceramic art is not that of painting, sculpture, pure design, or metal-like work; it is not possible to distinguish between the "ideal" and the "practical" piece of ceramic ware. (5) Broadly, ceramics should deal with masses; a certain restraint is necessary in the use of the effects of "patina" and reflec-

tions, which are often the result of chance or accident. (6) Beauty, clear or indistinct, can be found in simple, solid, useful things. (7) The collaboration between artist and artisan is necessary and desirable, but the artist must take into account the limitations of the medium and craft and must endeavor to conceal the effort of the workman and to illuminate the object, reanimate it, and give it intelligible and new clarity. The first prize was given for a vase with a black ground decorated with a gold rose and other colors. The purpose of the contest is discussed. Illustrated. M.V.C.

Glazed stones. H. C. Beck. *Ancient Egypt and the East*, 1931 and 1932; *Jour. Soc. Glass Tech.*, **22** [92] A288 (1938).—B. deals with glazed steatite ornaments found in Egypt, India, and Mesopotamia. Methods of production are described. Microscopic sections show that glazing substances altered the nature of the stone, rendering it hard, white, and opaque. Some glazes are glassy; others contain crystals of mullite, probably owing to the feldspathic nature of the glaze. Iron oxide was a common coloring agent, used in the clay or in the form of a salt; it apparently was not hard fired, as some of the color is still soluble in pyridine. Glazed quartz ornaments from Egypt, Mesopotamia, India, and Persia are described. Pale blue beads are colored with a glaze, which, according to H. Jackson, contains copper and soda. The glazes always contain soda but no lime. Deep blue glazes apparently contain cobalt, while some intense red ones are due to copper (*Ceram. Abs.*, **11** [4] 223 (1932)). Carnelians, agate, and feldspar are also discussed; carnelians are apparently whitened with soda. Many experiments were made by B. to reproduce the effects obtained by the ancients with indifferent results. Illustrated.

Pottery at Monte Alban. C. C. Dauterman. *Sci. Monthly*, **46** [2] 157–65 (1938).—The recent findings of pottery at Monte Alban, Mexico, are discussed from a cultural standpoint. Five distinct ceramic epochs are distinguished by differences of form, color, polish, ornamentation, etc. Illustrated. H.E.S.

BOOK

Keramic Kilns. Denver Fire Clay Co. and Hewitt Wilson. *Denver Fire Clay Co. Bull.*, No. 361, 57 pp. (1938).—This brochure describes kilns for pottery and china firing and development work. A treatise by W. on ceramic procedure covers clay preparation, casting slips, methods for shaping ware, drying, firing, engobes, and glazes. The design of and equipment for studio and pottery kilns are exhaustively illustrated and described. The booklet is a valuable addition to the library of any potter and especially the studio potters. R.C.P.

PATENTS

Decorating and writing on iron enamels, glass enamels, and glazes. Deutsche Gold- & Silber-Scheideanstalt vorm. Roessler. Ger. 666,230, Sept. 22, 1938 (Feb. 25, 1936); VI/48*c*. 3. Ceramic colors containing mineral oils or oils extracted from coal-distillation products, used alone or mixed together, especially colors mixed with a mixture of petroleum and lubricating oil, are rubbed on the unfired enamel or unglazed layer and fired with this layer in a single firing. D.A.B.

Designs for:

Bottle. A. I. Lorenzen (Owens-Illinois Glass Co.). U. S. 113,045, Jan. 24, 1939 (Nov. 21, 1938).

Bowl. W. K. Titze (Universal Potteries, Inc.). U. S. 113,024, Jan. 24, 1939 (July 1, 1938).

Cup. M. C. Ruskin. U. S. 113,017, Jan. 24, 1939 (Aug. 27, 1938).

Goblet. A. J. Cunningham. U. S. 112,988, Jan. 24, 1939 (April 28, 1938).

Jar. C. R. Underwood. U. S. 113,055, Jan. 24, 1939 (Nov. 19, 1938).

Plate. Frank Guildford (Scammell China Co.). U. S. 113,306, Feb. 14, 1939 (Oct. 25, 1938). A. M. Walker (Bailey-Walker China Co.). U. S. 113,311, Feb. 14, 1939 (Dec. 29, 1938).

Stemmed goblet. G. S. Bryce (Bryce Bros. Co.). U. S. 112,984, Jan. 24, 1939 (Nov. 26, 1938).

Tumbler. E. W. Fuerst (Libbey Glass Co.). U. S. 113,137 and 113,138, Jan. 31, 1939 (Nov. 21, 1938).

Whiskey glass. G. S. Bryce (Bryce Bros. Co.). U. S. 112,983, Jan. 24, 1939 (Nov. 26, 1938).

Cements

Application of X-ray methods in cement research. E. Brandenberger. *Schweiz. Arch. Angew. Wiss. Tech.*, **3** [9] 6 pp. (1937); *Eidgenöss. Materialprüfungs- & Versuchsanstalt Ind., Bauw. Gewerbe Zürich, Ber.*, No. 114, pp. 17–22 (1938); *Chem. Abs.*, **32**, 6825 (1938).—X-ray methods can be applied to studies of the determination of clinker minerals, changes of the mineral constituents in cement caused by chemical reactions and changes in modifications due to firing, setting, aging, etc., determination of the crystal structure of cements, and the formation of new crystalline compounds. Examples are given of X-ray analyses of various forms of $2CaO \cdot SiO_2$, mixtures of α-$2CaO \cdot SiO_2$ and $3CaO \cdot SiO_2$, a cement for marine structures, and $3CaO \cdot SiO_2$ in various stages of hydrolysis and hydration.

Dehydration of gypsum. D. S. Belyankin and K. M. Feodot'ev. *Trudy Petrograf. Inst. Akad. Nauk S. S. S. R.*, No. 6, pp. 453–61; abstracted in *Referat. Silikatliteratur*, **5** [3] 5080 (1938).—To clear up the question of the character of the water and the mineralogical independence of soluble anhydrite, tests were made on the heating and dehydration of three specimens of well-crystallized gypsum from deposits in Sicily, Ohio, and Caucasus. The heat curves show two characteristic breaks according to the reactions (1) $CaSO_4 \cdot 2H_2O \rightarrow CaSO_4 \cdot {}^1/_2H_2O$ and (2) $CaSO_4 \cdot {}^1/_2H_2O \rightarrow CaSO_4$. Three horizontal intervals were observed on the dehydration curves: (1) ordinary temperature to 70°C (gypsum); (2) 70° to 90°C (hemihydrate); and (3) 90° to 200°C (soluble anhydrate). Optical examination of the preparations of soluble anhydrate before and after its rehydration in air into hemihydrate gave the following values: (1) $Ng^1 = 1.555$, $Np^1 = 1.544$ and (2) $Ng^1 = 1.542$, $Np^1 = 1.530$, *i.e.*, the first are considerably larger than the other two. All facts determined favor hydrates more than zeolitic character of the water in the hemihydrate; they also favor the relative independence of the soluble anhydrate. M.V.C.

Determination of free magnesium oxide. N. A. Toropov and P. D. Katzenelenbogen. *Tsement*, **5** [7] 41–43 (1938).—Finely ground cement raw materials (0.2 g.) are placed in a 100- to 150-cc. glass; 1 to 3 g. ammonium chloride is added, and 50 ml. of a mixture consisting of 5% glacial acetic acid and 95% anhydrous methyl alcohol are poured over it. The glass is covered by a watch glass and placed on a water bath heated below the boiling point. The solution is filtered, and the residue is washed 5 to 7 times with anhydrous methyl or ethyl alcohol and evaporated to dryness in a porcelain cup in the presence of HCl acid. The residue is burned to isolate ammonium chloride, treated with HCl acid, and analyzed as usual. P.B. & E.S.

Preparation of kiln feed at Leeds plant of Universal Atlas Cement Co. Anon. *Concrete, Cement Mill Ed.*, **47**, 102–103 (1939).—The preliminary ball mill, 8 ft. long by $9^1/_2$ ft. inside diameter, is in closed circuit with a rake classifier. Fines go to a bowl classifier, which is in closed circuit with a second ball mill like the first. Fines from this mill go to one of two thickeners and then to a storage tank. The two kilns are each 10 ft. in inside diameter and 300 ft. long. The kiln-drive motors use direct current, and each is driven by a separate generator. The speed can be varied between 10 and 100 revolutions per hour by varying the voltage from the generators. W.D.F.

Properties of celites. V. N. Yung and Yu. M.

BUTT. *Tsement*, **5** [7] 29–35 (1938).—Brownmillerite and celite (1 mol. $4CaO \cdot Al_2O_3 \cdot Fe_2O_3$: 1 mol. $3CaO \cdot Al_2O_3$) were obtained synthetically from C.P. components by sintering at 1350 ±10°, *i.e.*, below the melting point of brownmillerite; this shows that the reaction took place in the solid phase. Both compounds showed clearly defined hydraulic properties. With an excess of calcium oxide, samples of lower strength and varying volume are obtained. When $2CaO \cdot SiO_2$ is present, the sample has lower binding properties. In regard to stability to the action of salts, samples with or without $2CaO \cdot SiO_2$ dissociate in 3% N_2SO_4 and $MgSO_4$ solutions in 1 to 2 months and in $CaSO_4$ solutions in 3 to 5 months. In water containing CO_2, the stability of all samples increased up to 12 months. P.B. & E.S.

Enamel

Arc welding. A. F. DAVIS. *Concrete, Cement Mill Ed.*, **46**, 280–81 (1938).—Parts of rolled steel, cast steel, and cast iron can be repaired by electric arc welding at a cost of only a fraction of that of replacement. Arc welding can be used to build up worn parts, such as locomotive journal boxes, locomotive and car wheels, gear cases, and car-axle threads; to repair broken parts, such as pump casting and gear boxes; and to fabricate car bottoms, bumpers, and brake shoes. W.D.F.

Enamel technique and pickling. HEIMBERGER. *Beizerei* (in *Emailwaren-Ind.*, **15** [13]), **3** [3] 9–12 (1938).—The surface of tubular ware is greatly impaired for enameling by pickling; the disadvantage can be remedied by changing the enamel batch (borax addition); borax, however, is costly and must be imported. Nitric acid as corrosive is suitable under certain conditions. Equally good pickling results can be obtained by the Feracid (clean pickling) process. Primary and secondary surface cleaning is satisfactory, and residues from pickling are removed. M.V.C.

Fundamentals of color in porcelain enamels. ANDREW I. ANDREWS AND CARL H. ZWERMANN. *Jour. Amer. Ceram. Soc.*, **22** [3] 65–72 (1939).

Heat-resisting alloys in the vitreous enameling industry. G. C. STAUFFER. *Ind. Heating*, **6** [1] 67–70 (1939).—The best compositions for heating elements in enameling furnaces or for tools used in such furnaces are 80% Ni and 20% Cr; 35% Ni, 15% Cr, and the remainder Fe; and 60% Ni, 15% Cr, and the remainder Fe. Ni alloys are preferable because the lack of loose scale prevents spotting of the goods by oxide coming off the heating elements. The C content should always be as low as possible to prevent formation of Cr carbide in the elements between 1100 and 1600°F. If it is formed, it can be redissolved by heating to 2000°F for about 1 hr. and quenching in water. M.H.

Increase of gas opacification to make the enamel whiter. W. O. *Emailwaren-Ind.*, **15** [27] 183–85 (1938).—O. discusses gas opacification produced by volatile gases present in the melt. This effect is produced by additions of fluorides, such as fluorspar, cryolite, and sodium silicofluoride. M.V.C.

Means for the suspension of enamels. ANON. *Glashütte*, **68** [41] 716–17 (1938).—The use of electrolytes, especially sulfates, should be avoided as much as possible. A good enamel consistency should be assured by rational grinding and by control, before the discharge of the mill, of fineness of the grains and specific gravity of the suspension. With well-conducted grinding, the addition of salts can usually be avoided. When a liquid enamel has thickened or hardened by long storing, it must be reground for an hour or less, and its suspension must be regulated by the addition of 0.2% to 1% carbonate of magnesia. For colored enamels, a hot solution of borax is suitable as an electrolyte to improve suspensions. M.V.C.

Opacifiers and their rational use. HANS KOHL. *Emailwaren-Ind.*, **15** [29–30] 199–202; [31] 207–10; [32] 215–19 (1938).—The characteristics of tin oxide, antimony compounds, cerium oxide, zirconium oxide, and titanium oxide as opacifiers are discussed in detail. The latest experiments with gas opacification are analyzed. M.V.C.

Progress in the field of enamel research in 1937. C. R. PLATZMANN. *Chem.-Ztg.*, **62**, 780–83, 823–25 (1938).—Progress in enamel research during 1937 is reviewed under four headings: (1) raw materials, especially the use of ZnO with ceramic products; (2) the preparation, production, and characteristics of enamels, black enamels for cast iron, marble-like gray enamel, and acid-resistant enamel; (3) defects in enamels and their avoidance; (4) testing of enamels, control, constancy, stability, use of the microscope, measuring of strength of enamel, determination of resistance to shock, measurement of expansion of glass enamel from melting point to room temperature, etc. Handling of enameled objects, removal of enamel, and the mottling problem are also discussed. 91 references. See *Ceram. Abs.*, **17** [11] 349 (1938). D.A.B.

Protection of iron during pickling. ANON. *Céram., Verrerie, Email.*, **6** [9] 261–62 (1938).—Substances which diminish the action of the acid on the iron during pickling without interfering with the pickling itself are called inhibitors or limiters and include arsenic (whose paralyzing action on H_2SO_4 in the presence of iron was first noted in 1845), glycerine, naphthalene, creosote, and fatty acids. The mechanism of their operation is not clear, but a simple theory considers the additions as colloidal bodies whose particles have different electric charges. The newly immersed metal draws the suspended colloid in the bath, which deposits in a thin protective coat according to Andrews (*Ceram. Abs.*, **14** [7] 158 (1935)). Large quantities slow down pickling, which is due to the tendency of the colloid to protect metallic surfaces not perfectly clean. Advantages of this process are the reduction of defects in the enamel and economy in acid and metal. Before a limiter is adopted, it must be tested under the given industrial conditions. See "Inhibitors—," *Ceram. Abs.*, **17** [11] 348 (1938). M.V.C.

Review of the latest technical developments in the enamel industry. H. J. KARMAUS. *Emailwaren-Ind.*, **15** [35] 231–33; [36] 241–43; [37] 250–51; [38–39] 257–58; [41] 272–75; [42–43] 281–82; [44] 288–89 (1938).—K. discusses new methods of enameling, raw materials, opacifiers, equipment, and uses of enamel developed in 1937. M.V.C.

Synthesis of enamel. VIELHABER. *Emailwaren-Ind.*, **15** [22] 155–57; [25–26] 175–76 (1938).—The composition of enamels is discussed. M.V.C.

Welding silicon steels. Review of literature to July 1, 1937. W. SPRARAGEN AND G. E. CLAUSSEN. *Welding Jour.* [N. Y.], **17** [9] Supp. 1–7 (1938).—The review includes a summary and an introductory discussion from the data on physical properties, recovery and pickup of Si in welding, fusion welding properties, resistance welding, forge welding, and flame cutting. It is not difficult to obtain high-strength welds in 1 to 2% Si steels with only fair ductility. The recovery of Si in the weld is dependent on the C content and range of Si of the rod, recovery increasing with C and Si content. Difficulties in welding Si steels (more than 1% Si) and silicon structural steels (less than 0.45 Si and 1.0 Mn) due to cracking and poor fusion are detailed, and inconsistencies in the literature are shown. Five research problems are suggested. 66 references. W.H.B.

SEPARATE PUBLICATION

Lecture course on enameling iron: I, Historical notes on iron, steel, and enameling. INLAND STEEL CO. AND A. I. ANDREWS. Inland Steel Co., Chicago, 1938. 3 pp. The Bessemer and the basic open-hearth processes are used in making steel today, and continuous rolling mills capable of changing an 8-ft. ingot into a strip of steel 40 in. wide and a mile long in 3 min. have supplanted the hand-rolling methods formerly used. II,

Materials of which iron and steel sheets are made. 3 pp. The steel is a refinement of the iron produced by melting iron ore, found in open pits and deep shafts in the Lake Superior region, in blast furnaces with coke and limestone. A good coke should be uniform as to size and ash content and free from volatile material and should have a high percentage of fixed carbon, low sulfur and high strength, porosity, and cleanliness. **III, Making pig iron in the blast furnace.** 6 pp. For every ton of pig iron produced, the blast furnace uses approximately two tons of ore, one ton of coke, one-half ton of limestone, and four tons of air. Molten metal is drawn from the blast furnace at about 2700°F and is led into a refractory-lined ladle of about 120 tons capacity. This ladle is mounted on railroad trucks and carries the metal either directly to the open hearth or to the pig machine where it is cast into pigs. Controlling and recording instruments have taken the mystery out of the blast-furnace process until today the furnace is as scientifically operated as any machine in the steel mill. **IV, Open-hearth process in making enameling-iron and steel sheets.** 7 pp. The principal use of the basic open-hearth process is for eliminating a large amount of alloying elements which are present in the raw material charge. Pig iron containing about 7% of these objectionable metalloids is refined until the final product, enameling iron, contains only 0.1% of these elements, *viz.*, C, Mn, P, S, and Si. Limestone, steel scrap, and pigs make up the charge. At the end of a heat (14 hr.) the carbon has been converted to carbon monoxide; silicon, manganese, and phosphorus are held in the slag as compounds of calcium; and the sulfur is held in the slag in limited quantities by reaction with manganese and calcium. When the control laboratory reports a satisfactory analysis and the operator has determined that the bath is at the proper temperature, the iron is poured into ladles and transferred to the ingot molds. The ingots are taken from the molds in a white-hot condition and delivered to the rolling mills. **V, Continuous rolling of hot strip for enameling iron sheets.** 4 pp. About fifteen 8-ton ingots, 2 x 4 x 6 ft., make up one open-hearth heat. Ingots are reheated in soaking pits to the proper rolling temperature (about 2300°F) and then delivered to the slabbing or blooming mill. The slabbing mill delivers a long slab which is cut into smaller slabs five to eight feet long, depending on the gage of the metal to be produced. These slabs are then reheated to 2250°F in 3 hr. and passed through a No. 1 scale breaker which removes the heavy scale. The clean slab then begins its passage through four roughing stands and six finishing stands. The steel never widens as it is rolled out but fortunately only lengthens as the thickness is reduced. **VI, Pickling and cold rolling enameling-iron sheets.** 4 pp. The hot-rolled strip of enameling iron comes from the rolls at a speed of 500 to 1800 ft./min. Continuous pickling operation then removes the scale and rinses the strip. Pickled strips are coated with oil to protect the metal before the cold rolling to proper gage begins. Cold rolling in tandem mills is done at speeds of 400 to 1200 ft./min. The strip is then cut into sheets and normalized or annealed. F.J.Z.

PATENTS

Applying vitreous enamels. W. J. Scott (Western Electric Co.). U. S. 2,146,858, Feb. 14, 1939 (April 1, 1936). A method of applying a mat finish vitreous enamel comprises fusing flint and flux in predetermined proportions to form an enamel frit having a relatively high maturing temperature, forming a second enamel frit having a relatively low maturing temperature by fusing flint and flux in different proportions, applying both frits to a surface to be coated, and firing the coated surface at a temperature below the maturing temperature of the frit having the higher maturing temperature but high enough to fuse the frit having the lower maturing temperature.

Enameling heavy metals. Siemens & Halske A.-G. Ger. 666,929, Oct. 6, 1938 (Aug. 14, 1936); VI/48*c*. 1. In enameling heavy metals such as iron or iron alloys, the surfaces of the heavy metal are metallized with an alloy or plating of a light metal; this layer is then oxidized, and the metal is finally enameled. D.A.B.

Enameling metals. Akt.-Ges. der Emaillierwerke und Metallwaarenfabriken Austria. Austrian 153,-990, Aug. 10, 1938; 48*c*; *Chem. Abs.*, **32**, 9426 (1938).—A ground enamel is applied in known manner and dried. A covering enamel is then applied and dried, and the two enamel layers are secured by a single firing. Enamel compositions suitable for use in the process are described.

Furnace for smelting porcelain enamel, etc. Ferro Enameling Co. (England), Ltd. Brit. 499,179, Feb. 1, 1939 (May 11, 1937).

Method and apparatus for desurfacing ferrous metal bodies by means of oxidizing gas streams. Linde Air Products Co. Brit. 499,493, Feb. 8, 1939 (Oct. 24, 1936).

Opaque vitreous enamel and process of making. Ignaz Kreidl (Vereinigte Chemische Fabriken Kreidl, Heller & Co. Mfg.). U. S. 2,147,202, Feb. 14, 1939 (Nov. 25, 1931; renewed Dec. 5, 1936). A process for producing a vitreous enamel for iron ware, etc., comprises preparing a composition of matter containing siliceous materials, borates, and fluorine compounds, the amount of fluorine contained therein being at least 10% of the unfused raw mixture by weight, any amount of such fluorine present in excess of 5% being supplied by a fluorine compound other than cryolite, and adding to the frit during the grinding thereof, to form a slip, a substance adapted to evolve gas during the firing of the enamel, which gas remains in the enamel in the form of bubbles, thus effecting the clouding of the enamel.

Producing an enamel-like protective layer over another layer. Evert Verwey, Paul Christiaan van der Willigen, and Johannes Hoekstra (Philips Patentverwaltung G.m.b.H.). Ger. 666,930, Oct. 6, 1938 (Oct. 10, 1936); VI/48*c*. 3. In a method for producing an enameled protective layer, the materials to be used are applied in the form of a suspension over the base or underlayer by an electrophorus. A suspension produced from pulverized glass or glass-forming constituents is used, and the porous layer produced by the electophorus is heated, if desired, in a nonoxidizing atmosphere until a coherent glass layer is obtained. D.A.B.

Producing enamels stable to temperature changes. I. G. Farbenindustrie A.-G. and Eisenwerk Kaiserslautern. Ger. 666,778, Sept. 29, 1938 (Jan. 11, 1936); VI/48*c*. 2.01. A method for enameling on cast and malleable irons which is stable to temperature changes is described. Quartz glass or quartz ware is added to the mixture to be ground or added later in the ground state. D.A.B.

Glass

Attack of alkali solutions on glass and the effect of other ions. Geffcken. Read at meeting of German Chemists, Bayreuth, June, 1938; abstracted in *Chem.-Ztg.*, **62** [54] 480 (1938); see "Chemical—," *Ceram. Abs.*, **18** [2] 45 (1939). D.A.B.

Bottle breakage—causes and types of fractures. F. W. Preston. *Bull. Amer. Ceram. Soc.*, **18** [2] 35–60 (1939).

Bubbles and seeds in glass melted in tank furnaces. G. Yu. Zhukovskiĭ and V. V. Polyak. *Stekolnaya Prom.*, **14** [7] 11–14 (1938).—The formation of bubbles and seeds in glass melted by the Fourcault method in Russia is discussed. M.V.C.

Calculation of the physical properties of glass: II, Expansion and density. Pierre Gilard and Leon Dubrul. *Verre & Silicates Ind.*, **9** [3] 25–28; [4] 37–39; [5] 50–52 (1938).—The authors proposed a parabolic formula (*Ceram. Abs.*, **13** [9] 232 (1934)) for the calculation of the coefficient of expansion, $\alpha = \Sigma (ax + bx^2)$, and obtained a satisfactory agreement between measurements and calculations. Since then they have verified these

factors on newly published measurements. The errors found are given. In addition to the relation which seems to exist between the value of the metal and the magnitude of the expansion factor of the oxide, in every group of valences there seems to exist a parallelism between the expansion factor and the molecular weight of the oxide, as shown by a comparison table of factors relative to the oxides which belong to homologous series; the parallelism is sometimes direct (RO group) and sometimes inverse (R_2O group). Methods formerly used for calculating the density of glasses are criticized. The authors decided to study the calculation of the density on the same basis as that used for calculating the coefficient of expansion, *i.e.*, by the formula $\Sigma x/d = \Sigma(ax + bx^2)$. The coefficients are established in the same manner as those for expansion. For the basic figure, that corresponding to vitreous silica, 0.454, was adopted; the factors for soda were then determined. With the aid of the corresponding soda glasses, the coefficients of lime and lead oxide were calculated. The potassium series with, eventually, lime and lead permitted the coefficient of potash to be obtained. Those of the other oxides were successively established. Errors up to 2% can be expected although they usually do not exceed 1% under controlled conditions. Curves show measurements of the density and the action of the constituents of glass. The coefficients indicated are tabulated together with the specific volume of the free oxides (multiplied by 100), the latter being taken in the vitreous state. An examination of the table does not show any clear relation of the initial coefficient with the situation in the classification of Mendéléev, with the molecular weight, or even with the specific volume of the free oxide. For Part III see *Ceram. Abs.*, **17** [9] 301 (1938). M.V.C.

Causes of optical impurity in glass. ANON. *Glashütte*, **68** [34] 577–78 (1938).—The origin of optical impurities (places having a different refractive power from the surrounding glass mass) is explained by the differing migration velocity of the glass components. Variations in the working conditions cause such defects. Analyses attempt to show this differing migration velocity as variations in the composition in the case of defects such as striae, bars, wave crests, and wave troughs. M.V.C.

Chemical-technological progress in the glass industry. RUDOLF SCHMIDT. *Chem.-Ztg.*, **62** [4] 37–40 (1938).—Progress in the glass industry during the last few years is reviewed in respect to the use of raw materials, introduction of rare-earth oxides, formulas, and melts. D.A.B.

Christmas tree glass. ANON. *Glass Ind.*, **19** [12] 459–61 (1938).—The Heidt Ornament Co., Brooklyn, N. Y., was the only manufacturer of Christmas tree ornaments able to compete with the foreign makers until the trade agreement with Czechoslovakia compelled it to change its product or close up. Business was partially saved by the production of Snow White and the Seven Dwarfs. The technique used in making them is described in detail. Illustrated. E.J.V.

Coloring agent in the so-called carbon yellow glasses: I, Coloring glass with colloidal carbon. C. NEUMANN AND A. DIETZEL. *Glastech. Ber.*, **16** [12] 389–91 (1938).—By the use of practically iron- and sulfur-free ingredients and by adding pure carbon, no yellow-colored melt was obtained. With measurable iron content but no sulfur, no yellow or brown colors resulted. Iron- and sulfur-containing melts show carbon yellow colorations with reducing agents other than carbon. Iron-free sulfur containing melts could also be obtained with a yellow color under reducing conditions. J.F.H.

Comparison of thermal expansions of glasses. A. E. BADGER AND J. F. WHITE. *Glass Ind.*, **19** [12] 463–64 (1938).—As there was no literature on the thermal expansions of glasses containing equivalent units of various oxides which can be incorporated in glass, a series of glasses was planned in which oxides would be introduced in a soda-lime-silica glass. The base glass chosen had the chemical composition $17.4Na_2O$, 10.1CaO, 72.5% SiO_2 (or $1.4Na_2O$, 0.9CaO, $6.0SiO_2$, on a molal basis). Additions of oxides were made to the glass batch in such amounts that equal numbers of atoms of the various elements were added to the base glass. The thermal expansions of the glasses were determined by the interferometer method. If thermal expansion factors on a weight-percentage basis are calculated from the experimentally determined expansions and from the calculated chemical analyses of the glasses, an expansion series may be arranged to show the relative effects of adding equal percentages of the oxides to these glasses. The oxides are listed in order of expansion produced, the oxide producing the greatest expansion being first: oxides of Li, Na, K, Mn, Pb, V, Mg, Ba, Fe, Ca, Ni, Co, Ce, Zn, Si, Ti, Zr, Al, and B. See "Thermal—," *Ceram. Abs.*, **16** [9] 272 (1937). E.J.V.

Crystallization phenomena in nephelite glasses. D. S. BELYANKIN AND V. V. LAPIN. *Trudy Petrograf. Inst. Akad. Nauk S.S.S.R.*, No. 9, pp. 3–21 (1936); *Mineralog. Abs.*, **7**, 140 (1936); *Chem. Abs.*, **32**, 8090 (1938).—In nephelite glass, soda and sulfate are partly replaced by nephelite or nephelite-syenite. Examination of fragments containing relict crystals of nephelite showed that these often exhibit vitrification and development of a comb-like or sieve structure. Radially fibrous albite was sometimes found. Devitrification of the glass resulted in the formation of pseudowollastonite and devitrite. Scaly cristobalite replaces quartz, and dendritic cristobalite is formed in the glass.

Decolorizing glasses with fluorine compounds. J. ENSS. *Glastech. Ber.*, **16** [12] 387–89 (1938).—The color of glasses containing ferric iron is decreased by adding NaF to the melt. The color intensity of ferrous-containing glasses seems to be unaffected. The effect is not due to loss of iron by volatilization. The behavior is compared with analogous behavior in an aqueous solution, and the possibility of the formation of complexes is discussed. J.F.H.

Dissociation of silicates and refining of glass. V. V. VARGIN. *Stekolnaya Prom.*, **14** [7] 15–17 (1938).—Bubbles present in optical glass are caused principally by secondary seeds which are separated during the cooling of the glass. The chief cause of these seeds is carbonic acid absorbed by the glass during cooling. Carbonic acid and some other gases are absorbed by the free basic oxides (Na_2O, BaO) and form chemical compounds (Na_2CO_3, $BaO \cdot BaCO_3$) which are stable at the high temperatures of the furnace atmosphere. Free basic oxides are formed during the dissociation of silicates: $R_2(Ba)SiO_3 \rightleftarrows R_2(Ba)O + SiO_2$. When temperatures decrease, a reversed process of silicate formation takes place with a separation of carbonic acid in the form of secondary seeds of carbonic acid or other absorbed gases. A rational melting should include a rapid increase of temperature for the thermal dissociation of the remaining carbonic compounds and the refining of the glass and a sharp lowering of the temperature below the temperature of silicate dissociation. M.V.C.

Elastic properties of Jena glasses. D. KUNERT. *Glastech. Ber.*, **16** [12] 383–86 (1938).—The density, elastic modulus, torsion modulus, and Poisson's ratio are tabulated for 155 Jena glasses. The elastic constants were determined by the method of Schaefer, Bergmann, and Goehlich (*Ceram. Abs.*, **17** [5] 177 (1938)) with an accuracy of approximately 0.5%. The glasses represent 22 types according to the Jena classification. The values varied for Poisson's ratio from 0.1945 to 0.2839; for torsion modulus from 1635 to 3596 kg./mm.^{2}; and for modulus of elasticity from 4090 to 9151 kg./mm.^{2}. The torsion and elastic moduli were notably lowest for some glasses of the FK type, while the highest Poisson's ratios resulted from low SiO_2 glasses of the KzFS type. J.F.H.

Feeding batch to tank furnaces. V. C. FUGMAN AND H. I. VORMELKER. *Glass Ind.*, **19** [6] 213–14 (1938); *Ceram. Ind.*, **30** [6] 39–41 (1938).—Advantages of mechanical batch feeders are enumerated, and designs are discussed. The type used at the Pitney Glass Works, Incandescent Lamp Dept. of the General Electric Co., Cleveland, Ohio, consists of three hoppers containing mixed batch which feed the batch through water-jacketed barrels by helical screw conveyers. The life of the feeder

screw and barrel depends largely upon the amount of cullet in the batch, as it exerts abrasive action on the metal. Operating data and details are given. E.J.V.

Fluorescence analysis in ultra-violet light. JULIUS GRANT. *Glass Ind.*, **19** [10] 387–89 (1938).—The principle of this method is based on the fact that many substances (including glasses) which appear identical in ordinary visible light, *e.g.*, daylight or lamplight, fluoresce differently when compared in ultra-violet light. Apparatus needed to produce ultra-violet light and filter glasses to separate visible and ultra-violet light are described. In testing, the glass is exposed to filtered light from the lamp (preferably in a darkened room), and the color and intensity of the resulting fluorescence are observed. The difference between two glasses may be one of intensity or one of color. An important application of the method is in the identification of glasses. E.J.V.

Fluorescent lumiline lamps. WARD HARRISON. *Glass Ind.*, **19** [5] 185–86 (1938).—Fluorescent lumiline lamps give up to 120 times the illumination, for current consumed, given by filament lamps of the same color with only a fraction of the heat. Fluorescent powders compounded and specially heat treated at the Nela Park laboratories control the color-producing qualities. Activated by ultra-violet and functioning as transformers, the powders absorb the short, invisible ultra-violet rays and reradiate this energy in the higher wave bands that comprise the color range of the spectrum. Each powder has its own characteristic wave band with which it responds to the ultra-violet, thus forming its own particular color of emitted light. The daylight and white colors will be of aid in color discrimination and color-matching work. E.J.V.

Gases in glass. S. E. KRASIKOV. *Stekolnaya Prom.*, **14** [7] 21–26 (1938).—K. gives a detailed discussion of American, English, German, and Russian studies of gases found in glass. The process of the discharge of gases from glass is very complex; it is not identical for all types of glass and depends on the physical dissolving of gas, saturation and oversaturation, and thermal disintegration, possibly related to the complex phenomena of molecular regrouping of the various compounds forming glass. M.V.C.

Glass fiber gaskets. ANON. *Mill & Factory*, **23** [6] 120, 122 (1938).—A woven glass fiber gasket for acid-resistant seals in chemical work (except HF) is described. The gasket is nonabrasive. D.A.B.

Glass fibers: production, characteristics, and applications. EUGENIO LOMBARDI. *Industria*, **52**, 3–8 (1938); *Chem. Abs.*, **32**, 9419 (1938).—L. gives the history of the fabrication of glass fibers with greater stress on the recent methods of production which have made this industry possible. He discusses the characteristics of glass fibers, the products made from them, and their uses.

Glass textiles to be manufactured by Owens-Corning Co. ANON. *Mill & Factory*, **23** [6] 100 (1938).—Fiberglas will be used in glass-insulated stoves and refrigerators and as insulation, material for protecting plants and shrubs, and separating plates for batteries. D.A.B.

Glass thread, yarn, and tape for electrical insulation. ANON. *Nat. Glass Budget*, **53** [29] 1, 10, 18 (1937).—All types of cables can be insulated with fiber-glass materials. They can be used in all types of electrical equipment (meters, transformers, and power reactors). H.E.S.

Glass threads and fibers. A. BRELAM. *Rusta-Rayonne*, **13**, 117–25 (1938); *Chem. Abs.*, **32**, 7689 (1938).—B. describes and discusses production and use.

History of flat glass in the United States. ANON. *Nat. Glass Budget*, **53** [17] 1, 8, 13, 18; [18] 1, 8, 9, 12, 16 (1937).—An extensive and accurate survey covers the principal producing and trading countries with particular reference to factors essential to tariff consideration. H.E.S.

Hollow glassware fused in tanks. ANON. *Verre & Silicates Ind.*, **9** [34] 391–92 (1938).—The simultaneous addition of alumina, boric acid, and baryta to the vitrifiable mix increases the fusing capacity of the furnace, makes the flux more homogeneous and better, and stabilizes the physical properties of glasses during working and when finished. Although the production of these new glasses involves a certain additional expense, economic and technological factors have forced industrialists to improve their products. Because of their slightly lower silica content, there is less risk with these glasses of (1) devitrification, (2) contamination of the flux by scum, (3) deformation of pressed objects during transfer, (4) poor lettering or relief designs, etc. The addition of 6 to 7 kg. feldspar to 100 kg. sand increases resistance to atmospheric agents, while 2 to 3 parts boric acid to 100 parts sand improves physical qualities and brilliance; 1 kg. baryta to 100 kg. sand favors fusion and homogeneity. M.V.C.

Importance of the electric furnace in the glass industry. SUTTOR. *Elektrowärme*, **8** [12] 301–308 (1938).—S. gives a definition of glass, a description of its manufacture, and brief historical data and discusses the use of electric furnaces in glassmaking. The electric furnace is used exclusively (in Germany, at least) for the production of silicon glass and safety glass and is being used more widely for annealing and decorative firing. It is used for melting only ordinary and lead glasses. The most suitable type is the resistance furnace; heating elements, metallic or nonmetallic, have been developed which will stand 1450°C permanently and which are resistant to reactive atmospheres. Formulas for calculating the economy and cost of operating an electric furnace, taking into account local conditions, are developed. M.H.

Industrial glass. W. A. KATES. *Chem. & Met. Eng.*, **45** [11] 603 (1938).—K. discusses the industrial uses of glass materials, *e.g.*, in filters, centrifugal pumps, etc. See "Commercial—," *Ceram. Abs.*, **16** [6] 170 (1937). B.C.R.

Influence of magnesia on the devitrification of soda-lime glasses. A. DIETZEL. *Glashütte*, **67** [2] 23 (1937); *Glass*, **14** [2] 60 (1937).—In soda-lime glasses, magnesia can be substituted for the lime, within certain limits, with a resultant lowering of the working temperature of the glass and an apparent lessening of the devitrification tendency. M.C.S.

Influence of small additions of certain glass formers on the course of fusing and on the characteristics of the glass. F. H. ZSCHACKE. *Chem.-Ztg.*, **62** [90] 812–13 (1938).—Z. compares the addition of small amounts of certain materials to glass melts to the addition of certain metals to alloys. The melting, refining, treatment, adaptability, and properties can be changed in the case of glass as in the case of metals. Some substances are purposely put into the formula and other materials get into the melt by accident. CO_2, H_2SO_4, and water are examples of the latter. CO_2 and water result from material impurities; H_2SO_4 results from SO_2 in gases. Arsenic affects color and tends to produce turbidity; alumina reacts on the chemical stability of glass; borax affects the coefficient of linear expansion; magnesium oxide affects the application of the glass; barium oxide is used for crystal glass; and zinc oxide is used for turbid glass. These materials produce these results when used in amounts of 1% or less; in other amounts, there are other or no changes. Z. gives the analyses of seven glasses and the influence of the different trace constituents. D.A.B.

Japanese glass history. ANON. *Nat. Glass Budget*, **52** [14] 1, 8, 9, 12, 13, 16, 17 (1937).—The developments and trends in the glass industry of Japan are given. H.E.S.

Modification of the shade of white and colored glasses under the effect of daylight. J. LÖFFLER. *Fachausschussber.* [Deut. Glastech. Ges.], **1937**, No. 41, pp. 1–8; *Chimie & Industrie*, **40** [1] 91 (1938); *Chem. Abs.*, **32**, 9417 (1938).—Hollow, transparent, light-resistant glass is obtained by clarification with As only provided there is added to the charge 6 to 7 kg. minium per 100 kg. of sand. In practice only glasses decolorized with Se or with pyrolusite are resistant to light. Ce glasses are stable toward light if a low-Mn lime is used and provided the charge is free from As. Glass can be decolorized with Ce and pyrolusite, the treatment being completed by physical decolorization by means of light. As it comes out of the annealing oven,

the glass is yellowish; it decolorizes in 2 to 4 weeks (according to the season) and then remains stable toward light.

I, Partnership of Carl Zeiss and Ernst Abbé up to 1880. II, Outcome of the partnership of Carl Zeiss and Ernst Abbé. III, Ernst Abbé as director of the workshop until his death. M. VON ROHR. *Forsch. Geschichte Optik*, **2** [2] 160–76; [4] 253–92; [5] 295–345 (193)8.—R. presents a history not only of the world-famous Zeiss Optical Company in Jena but also of the development of glasses and lenses in general. He gives testimony of the wonderful coöperation, coördination, and subordination under common aims which united these two men as friends and coworkers, each in his own field, for a life span full of successes which were only the logical sequence of loyal friendship in science and technique. The development of optical instruments and lenses is described. Regardless of recognition and financial rewards, these men remained modest characters; a human document of the highest type is the letter in which Abbé submitted to the government of the University of Jena his resignation as paid professor because the greater activity which the growing optical firm required of him was not reconcilable with his professorship. He asked, therefore, to be permitted to continue his courses at the university without pay and to use the income which he drew as director of the astronomical observatory for the purposes of that institute. They fulfilled their social obligation to their coworkers by creating the Carl Zeiss Foundation which not only secures the welfare of the workers during and after their active time with the firm but also provides means to further scientific research in the laboratories and shops of the Zeiss Co. as well as in the glassmelting firm of Schott & Gen. See "Optical—," *Ceram. Abs.*, **14** [9] 214 (1935); "History—," *ibid.*, **16** [6] 170 (1937). M.H.

Polishing glass, quartz, and agate on a hard polisher. I. V. GREBENSHCHIKOV AND S. V. NESMELOV. *Jour. Opt.-Mech. Ind.* [U.S.S.R.], **5** [6] 18 (1934); *Brit. Chem. & Phys. Abs.-B*, **57** [10] 1159 (1938).—The polisher is of glass, Ni, or cast Fe. Cr_2O_3, used as the polishing powder, is obtained by igniting $K_2Cr_2O_7$ with S, washing, and reigniting at a temperature suitable to the purpose required. Organic substances forming emulsions with H_2O are used for lubrication. See "Role—," *Ceram. Abs.*, **16** [4] 116 (1937).

Possibilities for using glass. G. SCHIEB. *Österr. Glaserztg.*, **3** [9–10] 82 (1938).—A glass roulette wheel is formed by machining a solid block. J.F.H.

Preston Laboratories. FRANK E. BARDROF. *Glass Ind.*, **19** [8] 301–303 (1938).—B. describes the new Preston Laboratories west of Butler, Pa., where fundamental research on the mechanical properties of glass and glassware and their behavior in breakage is being carried on. E.J.V.

Production, imports, and exports of plate glass. ANON. *Nat. Glass Budget*, **53** [22] 8, 17 (1937).—The annual production of polished plate glass in the U. S. from 1900 to 1936 and imports and exports are given. H.E.S.

Recuperative tanks at Fairmount Glass Works. ANON. *Glass Ind.*, **19** [12] 449–54 (1938).—A detailed description is presented of the recuperative tanks operated by the Fairmount Glass Works, Inc., Indianapolis, for more than six years, resulting in greater plant flexibility, reduction in space, and reasonable costs. E.J.V.

Red paint for glass. V. YA. LOKSHIN AND M. S. FEDOROVA. *Stekolnaya Prom.*, **14** [7] 31–33 (1938).—Paints used for glass are the easily melting lead or lead and borolead compounds with a pigment. This finely ground paint is applied on the ware and fired in muffle kilns at 550° to 580°. The compositions of several red paints developed in Russia are analyzed. M.V.C.

Relation between chemical composition and dielectric loss for the glasses R_2O–PbO–SiO_2, R_2O–CaO–SiO_2, and R_2O–B_2O_3–SiO_2. K. EGAMI. *Jour. Japan. Ceram. Assn.*, **42**, 619–28 (1934); *Brit. Chem. & Phys. Abs.-B*, **57** [8] 906 (1938).—Data are recorded.

Spectrometric identification of a gold-ruby glass. W. GERLACH. *Glastech. Ber.*, **16** [12] 391–92 (1938). J.F.H.

Strength of the chilled glass, Stalinite. K. T. BONDAREV. *Stekolnaya Prom.*, **14** [7] 28–30 (1938).—Data on the physical properties of the chilled glass, Stalinite, are given. M.V.C.

Strength of hollow glass vessels. K. H. BORCHARD. *Z. Ver. Deut. Ing.*, **82** [51] 1461–63 (1938).—In determining the resistance to fracture of glass bottles, new definitions were established. Pressure at rapid fracture, p_0, is called the highest inner pressure in atmospheres for rapid increase of pressure at which the bottle breaks, as contrasted to the endurance pressure, p_d, the highest constant inner pressure in atmospheres which the bottle will stand indefinitely without breaking. Pressure at fracture, p_z (instead of strength), is that pressure between p_0 and p_d which, after any duration of pressure, leads to fracture. The usual terms, tensile strength, compressive strength, and creep strength, mean material properties (load at fracture/section), while the new terms also include the influence of shape. Temperature at the time of testing and manner of holding the bottle in the testing machine are of great importance; the strength decreases with increasing temperature. Pressure at fracture, p_z, decreases with increasing duration of load according to the formula $p_z = p_0 (1 - c \log h)$, where p_0 = the pressure at rapid fracture, c = a material constant, and h = hr. For routine tests in the manufacturing process, a test of 1 hr. under 10 atm. pressure is sufficient. The strength of the glass can be increased by etching. Spheroidal and pear-like shapes are stronger than cylinders. The characteristic forms of fracture usually occurring are illustrated. Five references. M.H.

Structure of glass and methods of its investigation by X-ray analysis. A. I. KITAĬGORODSKIĬ. *Uspekhi Fiz. Nauk*, **19**, 201 (1938); *Jour. Soc. Glass Tech.*, **22** [92] A229 (1938).—K. gives an account of the recent concepts of the amorphous vitreous state of matter advanced by W. Zachariasen, G. Hagg, and W. Weyl. He believes that the statement of J. Randall, H. Rooksby, and B. Cooper (confirmed by N. Shishakov's investigations) regarding the existence of submicroscopic crystallites in glass was disproved by the recent researches of B. Warren. The X-ray investigations carried out on vitreous SiO_2 and B_2O_3 as well as on soda-silica and lead-silica glasses are described.

Structure of glasses. W. NOWACKI. *Schweiz. Arch. Angew. Wiss. Tech.*, **4**, 197 (1938); *Chem. Abs.*, **32**, 9417 (1938).—N. discusses crystal structures.

Summary of new developments in glass. R. A. MILLER. *Nat. Glass Budget*, **53** [7] 1, 12, 13, 18 (1937). H.E.S.

Three phases of glass: solid, plastic, liquid. P. BARY AND J. HERBERT. *Compt. Rend. 17me Congr. Chim. Ind.*, **1937**, pp. 1030–34; *Chem. Abs.*, **32**, 6817 (1938).—The period of plasticity exists between two transformation points about 350° to 450° apart. From measurements of the deformation and viscosity of glass, these two points can be calculated, and their variation with variation in composition of the glass can be studied. Difficulties encountered in interpreting the results of experiments already carried out are due to the fact that no account was taken of the time of heating, which renders it advisable to carry out additional investigations. See "Plasticity—," *Ceram. Abs.*, **17** [5] 180 (1938).

Tolerance control made easy in glass containers. J. W. SIEVERLING. *Nat. Glass Budget*, **52** [45] 3, 8, 17 (1937).—S. describes modern weighing equipment which is responsible for saving materials, controlling color and shipping weight, meeting strict capacity content specifications, and holding the customers' good will. H.E.S.

Views on the nature of glass from the Middle Ages to the beginning of the 19th Century: I–II. W. GANZENMÜLLER *Glastech. Ber.*, **16** [11] 358–65; [12] 392–98 (1938). J.F.H.

BOOKS AND SEPARATE PUBLICATIONS

Glass and Windows (Glas und Fenster). OTTO VÖLCKERS. Bauwelt-Verlag, Berlin, 1939. 128 pp., $8^1/_2$ x $11^1/_2$ in., 178 illustrations. This beautiful volume, distributed as a souvenir by the German Association of Flat Glass Manufacturers, is an outstanding example of fine

printing. A clear, simple type face has been used, set in single column with a $6^1/_2$ in. line. Calendered book paper brings out the full beauty of the illustrations, principally halftones from excellent photographs. One of these, almost startling in its reality, shows 16th-Century glass-blowers making disks of crown glass. It is photographed from a life-size model in the German Museum in Munich. The wealth of photographs, well selected and perfectly reproduced, is the outstanding feature of the book.

The work is divided into three sections: (1) the nature and cultural history of window glass, (2) the development of the window in German home life and architecture up to 1900, and (3) the study of window lighting and the importance of windows in the present day. A two-page bibliography is included. Technically, the most interesting portions of the book are those which discuss the distribution of light in rooms as it depends upon the size, shape, location, and framing of the windows. Clever schematic diagrams and some of the photographs bring out these matters clearly. Heat insulation and short-wave transmission are also discussed.

Anyone interested in building construction, either industrial or domestic, from the standpoint of making the best use of glass for interior lighting and architectural beauty will find in this book many helpful suggestions and illustrations. The text is well written, and the material is nicely organized. The volume excels as a picture book, however, and makes us wonder why our own technical books can not be as elaborately printed and gorgeously illustrated as the lay periodicals are. Subsidy, in the form of a share in advertising appropriations, is a possible answer. S. R. SCHOLES

Outline of Glass Science: Vol. I (Grundzüge der Glashüttenkunde). E. O. SCHULZ. Verlag Die Glashütte, Dresden, 1938. 194 pp. Price 6.40 Rm. S. deals with the chief properties of glass, its raw materials and composition, and refractories used in the glass industry. M.V.C.

Physical and Chemical Properties of Glass. V. V. VARGIN, K. S. EVSTROP'EV, K. A. KRAKAU, J. M. PROK, AND A. J. STOYAROV. Publishing House of Light Industry, Leningrad, 1937. 199 pp., 133 figs. Price 6 R. 75 k. Reviewed in *Jour. Soc. Glass Tech.*, **22** [92] A293 (1938).—The authors discuss viscosity, mechanical properties, thermal properties, optical properties, coefficient of expansion, devitrification, stones in glass, durability, surface tension, electrical properties, and the coloring of glass.

Scottish and Jacobite Glass. ARNOLD FLEMING. Jackson, Son, and Co., Glasgow, 1938. xv + 196 pp., 4 figs., 57 plates. Price 25s. Reviewed in *Jour. Soc. Glass Tech.*, **22** [92] A290 (1938).

PATENTS

Apparatus for:

Cutting glass sheets. E. W. KEIER (Libbey-Owens-Ford Glass Co.). U. S. 2,146,373, Feb. 7, 1939 (Nov. 27, 1935).

Drawing sheet glass. SOC. ANON. DES MANUFACTURES DES GLACES & PRODUITS CHIMIQUES DE ST. GOBAIN, CHAUNY & CIREY. Fr. 828,955, June 7, 1938; *Chem. Abs.*, **32**, 7691 (1938).—An electrical heating system for the furnace compartment from which the glass is drawn is described.

Making glass threads. OSCAR GOSSLER GLASGESPINST-FABRIK G.M.B.H. Fr. 827,599, April 28, 1938; *Chem. Abs.*, **32**, 8095 (1938).

Manufacture of glass stopcock barrels. L. MELLERSH-JACKSON (Kimble Glass Co.). Brit. 499,479, Feb. 8, 1939 (Sept. 6, 1938).

Manufacture of hollow glass blocks. OWENS-ILLINOIS GLASS CO. Brit. 497,964, Jan. 11, 1939 (July 2, 1936).

Apparatus and method used in tempering glass. GERALD WHITE (Libbey-Owens-Ford Glass Co.). U. S. 2,146,390, Feb. 7, 1939 (Feb. 29, 1936).

Device for producing calibrated glass tubes. CHRISTIAN KOB & CO. Ger. 665,943, Sept. 15, 1938 (April 11, 1936); VI/32*a*. 27. The device consists of a spreader which, when spread, contacts on all sides the inner wall of the tubes to be calibrated. D.A.B.

Electric furnace. W. W. TRIGGS (Y. R. Cornelius). Brit. 477,027, Jan. 7, 1938 (March 19, 1936).

Electric furnace for melting glass. V. F. FEENY (Soc. Anon. des Manufactures des Glaces & Produits Chimiques de St. Gobain, Chauny & Cirey). Brit. 498,379, Jan. 18, 1939 (Aug. 11, 1937).

Emergency stop for glassware-making machines. EDWARD MILLER (Lynch Corp.). U. S. 2,146,482, Feb. 7, 1939 (July 3, 1935); continuation of application Serial No. 661,915, March 21, 1933.

Forehearth for molten glass. BRITISH HARTFORD-FAIRMONT SYNDICATE, LTD. Brit. 498,204, Jan. 18, 1939 (April 1, 1937). W. T. HONISS (Hartford-Empire Co.). U. S. 2,144,973, Jan. 24, 1939 (April 1, 1937).

Glass-cutting board. A. P. CLAUSEN. U. S. 2,146,883, Feb. 14, 1939 (Nov. 24, 1937).

Glass felt. SOC. ANON. DES MANUFACTURES DES GLACES & PRODUITS CHIMIQUES DE ST. GOBAIN, CHAUNY & CIREY. Fr. 825,572, March 7, 1938; *Chem. Abs.*, **32**, 6824 (1938).—Glass fibers are impregnated with a binder such as latex before being subjected to a compressing action, *e.g.*, by passing between rollers, to form a thin felted sheet.

Glass furnace. SOC. CONTINENTALE D'APPAREILS MÉCANIQUES POUR LA VERRERIE (SOC. ANON.). Fr. 826,560, April 4, 1938; *Chem. Abs.*, **32**, 8096 (1938).

Glass press. V. L. NELSON (Hazel-Atlas Glass Co.). U. S. 2,146,346, Feb. 7, 1939 (Feb. 17, 1936).

Glass slabs for the construction of translucent walls, pavement lights, etc. P. CHINELLI. Brit. 497,991, Jan. 11, 1939 (April 12, 1938).

Glass threads. SCHLESISCHE SPIEGELGLAS-MANUFACTUR CARL TIELSCH G.M.B.H. Fr. 827,218, April 21, 1938; *Chem. Abs.*, **32**, 8096 (1938).—Glass thread for insulating wadding, cloth, cables, etc., is composed of concentric layers of glass of different compositions having different heat-expansion coefficients. Apparatus for making such threads is described.

Glassware. FRITZ CZULIUS. Austrian 153,664, June 25, 1938; 32*a*; *Chem. Abs.*, **32**, 7691 (1938).—Glassware carrying colored words or figures is made by superimposing colored glass layers in appropriate alignment on a sheet of glass, heating the sheet to its softening temperature, and uniting it with the glassware in the course of the manufacture of the latter. Methods of procedure are indicated.

Grinding machine for producing optical glasses (glasses with two focal points). RATHENOWER OPTISCHE WERKZEUGMASCHINENFABRIK MAX LINDEMANN. Ger. 667,933, Oct. 27, 1938 (Oct. 12, 1936); XII/67*a*. 19. D.A.B.

Hollow glass brick. H. FRIEDRICH. Brit. 498,284, Jan. 18, 1939 (June 7, 1937).

Hollow glass building block. B. F. HAZELTON, JR. (Owens-Illinois Glass Co.). U. S. 2,145,351, Jan. 31, 1939 (Sept. 11, 1936).

Infusion table for wire-glass production in glass-rolling machines. HEINZ SPIEKERMANN (A.-G. der Gerresheimer Glashüttenwerke vorm. Ferd. Heye). Ger. 665,942, Sept. 15, 1938 (May 3, 1937); VI/32*a*. 22. Wire reinforcement for sheet glass, consisting of single wires, netting, or gauze, is run through a slot-shaped opening inside of the rolling table; this slot-shaped opening runs in the same direction as the longitudinal axes of the rollers. D.A.B.

Joining metal to ceramic material. ALLGEMEINE ELEKTRICITÄTS-GES. Fr. 827,489, April 27, 1938; *Chem. Abs.*, **32**, 8098 (1938).—Particles of a metal such as Mo or W are fused into the ceramic surface and the metal is welded to this surface. Thus, powdered W is fused into a material of the composition MgO 30, SiO_2 61, Al_2O_3 4, CaO 2, and MnO_2 3%, and a piece of Fe-Ni alloy is joined thereto by a pure Ag solder.

Machine for laying out and marking ophthalmic lenses. O. M. SMITH. U. S. 2,146,599, Feb. 7, 1939 (Feb. 26, 1936).

Machine for the manufacture of glass bottles, etc.

F. W. Armytage. U. S. 2,147,393, Feb. 14, 1939 (Nov. 6, 1936).

Making glass tubes with exact inner shape. Felix Meyer. Ger. 665,944, Sept. 15, 1938 (March 28, 1936); VI/32*a*. 27. Addition to Ger. 642,907 (*Ceram. Abs.*, **17** [2] 68 (1938)).—The shape is produced by gradually introducing a tool into a softened glass tube (Ger. 642,907); during this process the glass tube is held in a position deviating from the vertical (preferably a horizontal position). D.A.B.

Manufacture of articles of fused silica, etc. General Electric Co., Ltd., J. H. Goodchild, and J. H. Partridge. Brit. 498,099, Jan. 18, 1939 (Dec. 8, 1937).

Manufacture of wire glass. Soc. Anon. des Manufactures des Glaces & Produits Chimiques de St. Gobain, Chauny & Cirey. Brit. 499,808, Feb. 8, 1939 (Feb. 5, 1937).

Mechanical transformation of glass tubes to glass cylinders of exact inside measurement. Felix Meyer. Ger. 666,267, Sept. 22, 1938 (Sept. 20, 1935); VI/32*a*. 27. D.A.B.

Method and apparatus for feeding molten glass. L. Mellersh-Jackson. Brit. 498,584, Jan. 25, 1939 (June 20, 1938).

Method and apparatus for forming pressed glassware. F. B. Dehn (G. M. S. Corp.). Brit. 497,889, Jan. 11, 1939 (Jan. 7, 1938).

Method and apparatus for perforating glass bodies. C. E. Hahn and P. P. Shebel (General Electric Co.). U. S. 2,146,572, Feb. 7, 1939 (March 18, 1936).

Method of capping vitreous vessels, such as electric incandescent lamps, without the use of cement. General Electric Co., Ltd. (Patent-Treuhand-Ges. für elektrische Glühlampen). Brit. 499,682, Feb. 8, 1939 (Nov. 12, 1937); addition to 467,956, July 7, 1937.

Phosphate glass. G. W. Johnson (I. G. Farbenind. A.-G.). Brit. 498,049, Jan. 18, 1939 (July 13, 1937).

Plastifiers. Consortium für Elektrochemische Industrie G.m.b.H. Fr. 827,658, May 2, 1938; *Chem. Abs.*, **32**, 8727 (1938).—Oxalic acid esters, particularly dibutyl oxalate, are used as plastifiers for polyvinyl acetate used as intermediate layers in safety glass.

Producing large castings from glass. Corning Glass Works. Ger. 666,990, Oct. 6, 1938 (Feb. 18, 1936); VI/32*a*. 24.04. The molten glass is poured into a movable form which is covered by a heatable hood or dome, and the filled form is removed from the hood and put into a cooling oven. D.A.B.

Producing tempered sheet glass of large dimensions. Compagnies Réunies des Glaces et Verres Spéciaux du Nord de la France. Ger. 666,861, Oct. 6, 1938 (Feb. 1, 1936); VI/32*a*. 30. Tempered sheet glass is produced from a rolled or drawn glass band which is tempered continually in direct connection with the production process. The glass band is reheated, after the cooling process, to the softening temperature in narrow zones in the range of lines provided for cutting, and then the glass is divided along these lines. D.A.B.

Production of covers with internal threads. Martin Fulda (Vereinigte Lausitzer Glaswerke A.-G.). Ger. 666,150, Sept. 22, 1938 (Feb. 19, 1937); VI/32*a*. 8. To produce the cover, a small ball of glass is partially blown up, and the bottom of the ball is put over a form provided with the threads. A second part of the form is applied to the outer part of the cover, and air is blown into the space formed by the outer and inner parts of the glass cover; this impresses the threads onto the inner wall of the hollow cover. D.A.B.

Production of fibers and threads from glass, slag, etc., meltable materials. N. V. Mij. tot Beheer en Exploitatie van Octrooien. Brit. 483,794, May 11, 1938 (Aug. 21, 1936).

Production of glass threads. O. Gossler Glasgespinst-Fabrik Ges. Brit. 498,707, Jan. 25, 1939 (Nov. 21, 1936).

Reinforced glass. Soc. des Usines Chimiques Rhône-Poulenc. Fr. 826,548, April 1, 1938; *Chem. Abs.*, **32**, 8097 (1938).—A sheet of glass is reinforced by a sheet of soft plastic material having a basis of cellulose derivatives having a thickness of the order of 1 mm. and more. The plastic material contains cellulose derivatives 45 to 66 parts and plastifier 55 to 34 parts, *e.g.*, cellulose acetate 58, triphenyl phosphate 8.4, Me phthalate 12.6, and triacetin 21%.

Safety glass. Kodak-Pathé. Fr. 826,739, April 7, 1938; *Chem. Abs.*, **32**, 8097 (1938).—Sheets of glass are assembled by an adhesive with an intermediate layer composed of an organic ester of cellulose of high viscosity and containing a high proportion of plastifier. The ester may be an acetate or a mixed ester of at least 500 sec., and the proportion of plastifier is 100 to 150% of the weight of the ester.

Safety glass. Libbey-Owens-Ford Glass Co. Fr. 827,410, April 26, 1938; *Chem. Abs.*, **32**, 8097 (1938).—Two sheets of glass are joined by an intervening sheet of plastic material composed of a resin resulting from the reaction of an aldehyde (CH_2O) on a polyvinyl ester hydrolyzed to give a product in which at least 60% of the utilizable OH groups have reacted with the aldehyde and an ester of sebacic acid acting as plastifier. The plastifier may be a dialkyl, dialkoxy, di(polyglycol ether), or di(tetrahydrofurfuryl) sebacate.

Safety glass. Libbey-Owens-Ford Glass Co. Fr. 827,411, April 26, 1938; *Chem. Abs.*, **32**, 8097 (1938).—The plastifier is an ester of a monohydric alcohol and a dicarboxylic acid of four or more straight-chain CH_2 groups, *e.g.*, Me or Et esters of adipic, sebacic, seberic, and decamethylene dicarboxylic acid. A phthalic acid ester may be added in each case.

Sealing electric conductors through glass. General Electric Co., Ltd. (Patent-Treuhand-Ges. für elektrische Glühlampen). Brit. 498,102, Jan. 18, 1939 (Dec. 13, 1937).

Table for cutting glass. Friedrich Pahmeier. Ger. 665,160, Sept. 1, 1938 (Dec. 19, 1936); VI/32*a*. 33. A table for cutting glass is provided with a sliding carriage for the straightedge which serves as a guide for the cutting tool; the sliding carriage is on a guide bar which runs parallel to the edge of the table. The carriage slides along this guide bar. D.A.B.

Tempering glass. André Citroën. Fr. 826,690, April 6, 1938; *Chem. Abs.*, **32**, 8096 (1938).—A localized tempering is obtained by placing the sheet of glass heated to a suitable temperature between two plates of refractory material with raised portions which enter into contact with the glass.

Tempering glass articles. J. T. Littleton (Corning Glass Works). U. S. 2,145,119, Jan. 24, 1939 (April 17, 1935). The method of tempering a glass article includes heating the article throughout its thickness to a temperature near the strain point of the glass from which the article is made, rapidly heating the surface of the article in a relatively short interval of time to a temperature well above the strain point of the glass, and chilling the article.

Tempering glass articles. C. J. Phillips (Corning Glass Works). U. S. 2,145,128, Jan. 24, 1939 (Nov. 11, 1936). The method of tempering a glass article includes heating it until its interior is at a temperature between the strain point and the softening point of the glass and chilling it in a liquid bath containing a molten alkali nitrate and a molten nitrate selected from the group consisting of alkaline-earth nitrates and lead nitrate.

Tempering glass articles. C. J. Phillips (Corning Glass Works). U. S. 2,146,224, Feb. 7, 1939 (Nov. 11, 1936).

Tempering glassware. Corning Glass Works. Fr. 828,939, June 3, 1938; *Chem. Abs.*, **32**, 7692 (1938).—Fused baths containing an alkali chromate are used as heating or chilling liquids in tempering glassware. Specified heating baths contain K_2CrO_4 50 and Na_2CrO_4 50% or K_2CrO_4 32.5 and KCl 67.5%. Specified chilling baths contain $K_2Cr_2O_7$ 85, Na_2CrO_4 13, and K_2CO_3 2% or $K_2Cr_2O_7$ 95 and SnO_2 5%. Other examples are given. As alternative chilling baths, use may be made of fused mixtures containing an alkali nitrate and a nitrate of an alkaline earth metal or $Pb(NO_3)_2$. Specified baths of this type contain KNO_3 42.5, $NaNO_3$ 37.5, and $Ba(NO_3)_2$ 20%

or KNO_3 80 and $Pb(NO_3)_2$ 20%. Other examples are given.

Tempering hollow glass articles. PILKINGTON BROS., LTD. Brit. 497,896, Jan. 11, 1939 (June 24, 1937).

Vertical retort settings for the carbonization of coal, etc., materials. F. J. WEST, E. WEST, AND WEST'S GAS IMPROVEMENT CO., LTD. Brit. 497,863, Jan. 11, 1939 (Aug. 18, 1937).

Vitreous enamel. GAMES SLAYTER (Owens-Illinois Glass Co.). U. S. 2,144,666, Jan. 24, 1939 (Aug. 6, 1936). The method of decorating a surface with an enamel coating of predetermined thickness comprises mixing with a vehicle an aggregate of granulated ceramic pigments comprising granules of graduated sizes, the largest being of a diameter or thickness substantially equal to the thickness of the coating, and the smaller granules being of such graduated sizes and in such proportions as to fill in the greater portion of the interstitial spaces between the larger granules and thereby form a dense mixture, applying the mix to the surface by a stamping implement, utilizing the largest granules as a spacing means to space the stamping implement from the surface which is being decorated a distance about equal to the diameters of the largest granules, and thereby determining the thickness of the applied coating.

Structural Clay Products

Brick-paved subway in Bucyrus, Ohio. ANON. *Dependable Highways*, No. 161, pp. 3–5 (1938).—Illustrated. P.S.D.

Brick pavement for airport. O. K. PHILIPP. *Dependable Highways*, No. 161, p. 7 (1938). P.S.D.

Determination of the mechanical strength of green brick. G. A. FLEISCH. *Zavodskaya Lab.*, **7**, 612–13 (1938).—The method consists in dropping the brick from a height of 1 m. and determining the loss in weight after each drop. The addition of sulfite-cellulose lye considerably increases the strength and contributes to the conservation of sharp edges and corners. P.B. & E.S.

Painting cement-asbestos compositions. ANON. *Nat. Paint, Varnish, & Lacquer Assn., Sci. Sect. Circ.*, No. 563, pp. 154–57 (July, 1938); *Brit. Chem. & Phys. Abs.–B*, **57** [10] 1163 (1938).—Two boxes made of corrugated asbestos cement were similarly exposed; the box painted white was 3° to 5° cooler than the unpainted box. The painted material absorbs negligible amounts of H_2O, whereas the unpainted composition absorbs 4 oz./sq. ft. of surface. Exposure tests with two coats of a green paint on a series of primers show that the material can be satisfactorily painted.

Temperature and humidity effects in unpainted and painted brick structures. ANON. *Nat. Paint, Varnish, & Lacquer Assn., Sci. Sect. Circ.*, No. 562, pp. 152–53 (July, 1938); *Brit. Chem. & Phys. Abs.–B*, **57** [10] 1163 (1938).—A graph and charts show temperature and relative humidity variations during the summer of 1937 in two penthouses. One of them was painted white and had a maximum temperature of 35° and a constant relative humidity; the other was unpainted and had a probable maximum temperature of 43°; the relative humidity varied from 55 to 70%.

SEPARATE PUBLICATION

Water permeability of masonry walls. CYRUS C. FISHBURN, DAVID WATSTEIN, AND DOUGLAS E. PARSONS. *Nat. Bur. Standards Bldg. Materials & Structures Rept.*, BMS7, 35 pp. Supt. of Documents, Govt. Printing Office, Washington, D. C. Price 10¢. Walls of brick, structural clay tile, and hollow concrete unit masonry were tested under conditions resembling exposures to wind and rain, and their resistance to the penetration of water was determined. Five kinds of workmanship (method of filling joints), three kinds of brick, six kinds of structural clay tile, two kinds of hollow concrete units, and six mortars were used in the construction of the walls. One group of 48 brick walls included specimens, both 8 and 12 in. thick, of three kinds of brick, four cement-lime mortars, and two classes of workmanship in all possible combinations. The walls of structural clay tile were faced either with stucco or with brick of a single variety. Those of concrete units were faced either with the same brick or with cement paint. The effectiveness of several methods of waterproofing was compared by retesting some of the walls after they had been treated. Treatments for the walls included the filling of openings in the face joints with mortar, grout, or wax and the application to the exposed surfaces of colorless solutions or paints. Most of the walls were subjected to water-penetration tests under two different conditions. Water was applied near the tops of the walls so as to produce a thin film of water over their exposed surfaces. In the capillarity test, no pressure was applied to the exposed face, the water penetrating under the forces of capillarity and gravity only. In the heavy-rain test, a static air pressure of 10 lb./sq.ft. was maintained against the exposed face. The performances of the walls in the water-penetration tests depended more upon the quality of the workmanship than upon any other factor. Walls of brick having the interior joints well filled with mortar usually gave excellent performances, whereas those with poorly filled joints leaked. Aids in obtaining walls resistant to moisture penetration are the use of mortars of medium or high water retentivity, the wetting of absorptive brick before use, and the application of a parging of mortar on the back of the facing wythe. The omission of two-thirds the normal number of header brick or the insertion of a limestone sill or belt course had no important effect on the permeability of the walls. On the average, walls with a brick facing and a backing of hollow masonry units were slightly less permeable than brick walls of equal thickness when the joints were not well filled. When the joints were well filled, the performance of walls with hollow units was somewhat superior in the capillarity test but inferior in the heavy-rain test to that for otherwise similar all-brick walls. The performance of walls of structural clay tile faced with Portland-cement stucco was somewhat better than the average for brick walls. The filling of openings in the joints with mortar, grout, or wax was effective in stopping leakage. Applications of colorless waterproofing solutions did not stop leakage through openings in the joints but improved the performance of absorptive brick when the openings in the joints had been sealed. Coatings of molten paraffin, oil paint, and cement paint reduced moisture penetration. R.A.H.

PATENTS

Building blocks for hollow walls. E. G. MILLER. U. S. 2,145,187, Jan. 24, 1939 (April 5, 1938). A hollow wall comprises inner and outer blocks, each having a plurality of horizontally and vertically spaced bosses on the inner surface thereof, and a partition in the wall separate from the blocks, between and in contact on opposite sides with the inner ends of the bosses of the respective blocks.

Building construction. P. P. STOUTENBURGH. U. S. 2,146,775, Feb. 14, 1939 (Jan. 27, 1938). A double wall building block construction includes above-soil and subsoil portions, the upper portions comprising a relatively nonporous outer wall and a relatively porous inner wall longitudinally spaced apart.

Ceramic products. HUBERT ZANOSKAR. Austrian 153,980, Aug. 10, 1938; *80f; Chem. Abs.*, **32**, 9425 (1938).—Tile, hollow ware, and other ceramic products are coated with a composition prepared by dispersing an allophanoid clay in water with the aid of a small proportion of an alkaline peptizing agent, *e.g.*, a caustic alkali and an alkali carbonate and (or) an alkali silicate. The composition may include a pigment and (or) colloidal SiO_2, and it may be boiled under pressure before use. The products to

which the composition is applied are afterward fired. Examples are given.

Device for producing grip holes on hollow brick or tile formed by the wire cutting press. EMIL NEUPERT. Ger. 667,578, Oct. 20, 1938 (April 1, 1937); VI/80*a*. 23.02. Grip holes are produced on tile or brick by a striking tool swinging on a lever around a shaft against the front side of the molded article. D.A.B.

Hardening porous hydrosilicate-bound blocks. YXHULTS STENHUGGERI AKTIEBOLAG. Brit. 498,483, Jan. 18, 1939 (July 16, 1936).

Production of hollow brick or tile. GUSTAV STANDKE. Ger. 664,978, Aug. 25, 1938 (May 30, 1936); VI/80*a*. 43.10. Hollow tile or brick closed on all sides is produced by using a sagger in which the brick or tile is formed by employing pressure from within the brick or tile. A preshaped hollow mass is repressed in a closed sagger by introducing air, gas, or steam pressure into the hollow space of the brick or tile. D.A.B.

Sand-facing of brick. R. T. L. SHORROCK. Brit. 499,527, Feb. 8, 1939 (Oct. 22, 1937).

Wall structure. J. M. PILLATZKE. U. S. 2,145,229, Jan. 24, 1939 (June 30, 1937). In a wall construction a plurality of block members disposed in superposed staggered relation, each of the block members comprising a solid intermediate portion and hollow outer portions, the outer portions extending above and below the upper and lower faces of the intermediate portion whereby to provide a longitudinally disposed channel on the upper and lower sides of each block member, the width of each of the outer portions being substantially equal to one half the width of the channel, and a jointing member engaging in the confronting channels of opposed block members having a length equal to the length of a block member, the jointing members of adjacent blocks being disposed in end-abutting relation and each jointing member having a thickness substantially equal to twice the depth of a channel in a block.

Refractories

Attack of refractory materials used in glassmaking. J. BAUDEWYNS. *Ing. Chim.*, **22** [131] 211–27 (1938); abstracted in *Verre & Silicates Ind.*, **9** [34] 395 (1938).—B. studied used tank block and the chemical composition of the 3 zones and determined the porosity of the unaltered refractories. He describes the corrosion phenomena as realized in the following stages: (1) penetration by capillarity, (2) chemical action whose extent is a function of that penetration. The numerical results of these analyses and the length of service of the block (ordinary 26, special 32, sillimanite 59, and Corhart 72% Al_2O_3) prove that compactness is the essential element of resistance while the high alumina content has only relatively little effect. Different clays (containing kyanite) were fired at rising temperatures, and the attack of Na_2CO_3 was determined by the method of Gehlhoff. Above 35% Al_2O_3, the loss is independent of the chemical constitution and depends on the compactness alone. Rational manufacture requires the use of a pure clay fired to its maximum density. M.V.C.

Bonding materials containing silica and silicates. H. W. WEBB. *Proc. Chem. Eng. Group, Soc. Chem. Ind.*, **19**, 86–89 (1937); *Brit. Chem. & Phys. Abs.-B*, **57** [8] 909 (1938).—The constitution and practical applications of typical refractory jointing materials, concrete, and cements for high and low temperature use are outlined briefly.

Chemical-mineralogical changes in Dinas brick from the roof of an electrical steelmelting furnace. V. V. LAPIN. *Trudy Petrograf. Inst. Akad. Nauk S.S.S.R.*, No. 7–8, pp. 235–36 (1936); *Mineralog. Abs.*, **7**, 139 (1936); *Chem. Abs.*, **32**, 8721 (1938).—Chemical and microscopic studies of used silica brick show a maximum concentration of Fe_2O_3, FeO, and MnO in the gray cristobalite zone and of TiO_2, Al_2O_3, and CaO in the transitional brownish zone. Cristobalite occurs as dendrites or scaly aggregates, often intergrown with magnetite and brown crystals of (?) monticellite (n 1.74). Brown (n 1.684) and yellowish (n 1.673) glass is present in the high-temperature zone.

Chemical and mineralogical characterization of a magnesite brick from the Iljitsch Factory in Mariupol. D. S. BELYANKIN AND B. V. IVANOV. *Trudy Petrograf. Inst. Akad. Nauk S.S.S.R.*, No. 11, pp. 111–26 (1937); abstracted in *Chem. Zentr.*, **1938, II**, 3298–99 (1938).—Magnesite brick from a Siemens Martin furnace were examined after operation. Four zones were differentiated, and an additional thin layer of magnesite was added to those in the upper part. In the 3 outer zones, monticelbite outweighed forsterite; in the 2 inner zones, the reverse was found. The outermost zone was practically unchanged; after it, the FeO content gradually increased. In the second zone from the outside the maximum TiO_2 and Al_2O_3 contents were found. M.V.C.

Concentration of refractory clays. A. N. IKONNIKOV. *Uralskaya Metallurgiya*, **1938**, No. 5, pp. 36–38.—I. studied the concentration of Ural refractory clays by various methods. Two samples were studied; one was contaminated chiefly by pyrite and quartz, and the other by spherosiderite. The process of concentration is described. B.E.K.

Effect of sodium aluminate on the thermal expansion of refractory clay bodies. W. R. MORGAN. *Jour. Amer. Ceram. Soc.*, **22** [3] 88–90 (1939).

Existence of siloxicon in SiC furnaces. A. DIETZEL AND W. STEGMAIER. Read at meeting of German Chemists, Bayreuth, June, 1938; abstracted in *Chem.-Ztg.*, **62** [54] 480 (1938). D.A.B.

Firebrick linings in the coke industry. S. HARTMAN. *Gaz & Woda*, **17**, 238–43 (1937); *Chem. Abs.*, **32**, 8724 (1938).—Quartzite fire brick were found to be the best lining when various linings were tested for fire resistance, constant volume, expansion, resistance to salts and acids, heat conductivity and content, sudden change of temperature, porosity, and mechanical durability.

Fused cement in refractory masonry. MARCEL LÉPINGLE. *Verre & Silicates Ind.*, **9** [10] 109–12 (1938).—Preliminary tests to further improve fused cement by changing the quality of the chamotte and by reducing the fusible elements showed that (1) replacing commercial fused cements by a theoretical cement free from secondary fluxes did not improve the behavior on firing; (2) the addition of a better chamotte considerably improved behavior on firing; (3) the addition of raw rock rich in alumina did not contribute to the desired result, in that the transformation kyanite–mullite takes place in its original situation and injures the solidity of the concrete; (4) the cement content of concrete can be limited about 10%. The composition of concrete is a function of the cost price of cement and chamotte, of the mechanical resistance to heat and cold, and of the temperature which this concrete must resist. Besides lowering the cement content, the lowering of the water content increases the mechanical resistance of concrete to heat. Granulometric composition is important. M.V.C.

Increase in durability of hearth brick of basic open-hearth furnaces. I. ANDREEV AND A. ZHURBENKO. *Stal*, **1937**, No. 1, pp. 17–32.—Previous observations established that (1) under the influence of the oxidizing action of the flame, crystals of magnesioferrite, which loosen the crystalline growth, are formed in the hearth brick of basic open-hearth furnaces and (2) as the new hearth brick is always porous, the first fusion gives a reduced productivity of metal. The hearth brick appears covered by metallic veins. It is supposed that by oxidation these veins of metals form slag which destroys the hearth brick. Pines ("X-ray—," *Ceram. Abs.*, **16** [9] 278 (1937)) established, however, that the grains of periclase are cemented by minerals formed by reciprocal action of periclase with various elements of open-hearth furnace slag. In the magnesite and dolomite hearth brick, these minerals are (1) monticellite, $(MgCa)_2SiO_4$, (2) olivine,

$(MgFe)_2SiO_4$, and (3) spinel, $MgO \cdot Al_2O_3$. In hearth brick of pure dolomite, calcium silicates (CaO) are also found. Freberg and Babus ("Highly—," *ibid.*, **15** [10] 304 (1936)) assume that pure forsterite ($2MgO \cdot SiO_2$) is also present. Monticellite, olivine, and spinel are formed by the dissolution of periclase in the slag of the open-hearth furnace and by later crystallization from the solution. The content of monticellite and olivine is proportional to the content of magnesium oxide and calcium oxide in the hearth brick. The orthosilicates of Fe, Mg, Mn, and Ca can form isomorphous mixtures of various compositions from forsterite to fayalite ($2FeO \cdot SiO_2$) and tephroite (Mn_2SiO_4). Wear of the hearth brick, therefore, results from the actions of slags which stimulate the process of overcrystallization. The acceleration or retardation of the process depends on the slags, if the initial growth is wear-resisting and if the working method and the construction of the hearth brick permit the rapid flow of the whole slag. The authors conclude that (1) the durability of hearth brick appears to depend on the crystalline growth of grains of periclase into the monolith, (2) the chief destroyer of crystalline cement is the slag of open-hearth furnaces, which stimulates the free grains of periclase, and (3) to increase the durability of hearth brick, it is necessary to increase the crystalline cement, to reduce the time of contact of the slag with the hearth brick, and to reduce the content of slag in the hearth brick. See *Ceram. Abs.*, **18** [2] 52 (1939). B.E.K.

Insulation computations. F. Peiter and M. J. Fish. *Combustion*, **9** [11] 31–34 (1938).—A method of computation for determining the insulation required for vertical walls of boilers is presented. The formulas are developed and explained, and typical examples are included to illustrate the use of the formulas. H.E.S.

Obtaining alumina by dissolving clay in hydrolyzing salts. N. S. Revina. *Acta Univ. Voronegiensis*, **9** [3] 21–28 (1937); *Chem. Abs.*, **32**, 7221 (1938).—When clay containing 35.85% Al_2O_3 is treated with 20% solutions of $FeCl_3$ at 100° for 1 to 12 hr., 33% of the Al is removed as $AlCl_3$. Removal is more complete with hydrolyzed $FeCl_3$ than with pure HCl. The $AlCl_3$ is converted to $Al(ONa)_3$ and precipitated by the addition of CO_2.

Refractories. Anon. *Times Trade & Eng.*, **44** [899] 21 (1939).—Improvements in refractory materials made in Great Britain in 1938 are summarized. A.B.S.

Refractory materials for glass furnaces. E. Preston. *Glass Rev.* (1936); *Experimental Researches & Repts.*, **19**; abstracted in *Refrac. Jour.*, **13** [10] 688 (1937).—P. refers to new types of fireclay, silica, and special refractories. He also deals with the corrosion, disintegration, physical properties, and testing of refractories. B.C.R.

Solubility and disintegration of aluminum oxides. G. F. Hüttig, G. Markus, and E. Franz. Read at meeting of German Chemists, Bayreuth, June, 1938; abstracted in *Chem.-Ztg.*, **62** [50] 445–46 (1938). D.A.B.

Spalling of silica brick during heating and cooling of furnaces. J. M. McKinley and S. M. Phelps. *Jour. Amer. Ceram. Soc.*, **22** [3] 83–88 (1939).

Steelworks refractories. T. Swinden and J. H. Chesters. *Iron & Coal Trades Rev.*, **136** [3662] 764–67; [3663] 824–26 (1938); see *Ceram. Abs.*, **17** [11] 355 (1938). M.H.

Stone tile and pottery plate. Fritz Kästner. *Sprechsaal*, **71** [32] 394–96 (1938).—The injurious expansion due to heat of potters grog is conditioned by the modification and transformation of the silicic acid (100° to 300° cristobalite and 400° to 500° and 500° to 600° quartz). The transformation of the silicic acid is easily determined by the specific gravity and data on the refraction of light. Measurements of the expansion due to heat and its mathematical value can easily lead to false conclusions. M.V.C.

Tendency of refractory blocks in glass furnaces to protect themselves and the conclusions to be derived. K. Pukall. *Glastech. Ber.*, **16** [11] 351–58 (1938).—The changes taking place in refractories in service are in the direction of more stable and corrosion-resistant forms. Photographs show how the zone of mullite formation in a clay refractory protects the refractory from further corrosion. In the preparation of refractories, conditions prevailing in tanks should be given more attention. Careful limits should be observed for clays suitable for pots and tanks, especially in relation to the fluxes present. Refractory clays should be carefully prepared before firing, *e.g.*, by grinding to insure uniformity. The greatest care should be used in firing to reach the point of formation of a vitreous bond between refractory grains and clay binder to avoid the dissolving out of the grains by the molten glass. To improve resistance to glasses of low surface tension, finer refractory grain sizes are recommended. The porosity of refractories could appropriately be further decreased, even at the cost of stability toward temperature change. Hartmann ("Action—," *Ceram. Abs.*, **17** [5] 185 (1938)) has shown that a porosity of 8% is most suitable in refractories for resistance to slag and soda attack. J.F.H.

Thermal conductivity of porcelain and kieselguhr brick up to 800°C. W. Koch. *Physik. Z.*, **39** [11] 431–36 (1938).—K. describes a method for determining the coefficient of thermal conductivity of ceramic bodies, heat-insulating materials, etc., at temperatures up to 800°C. The test piece consists of a block 100 x 100 mm. in area and 30 to 50 mm. high. The heat is supplied by an electric heater plate so arranged that heat losses are practically eliminated. The thermal conductivity is calculated from the readings of a Pt-Pt Rh thermocouple, the dimensions of the test piece, and the electrical power. Average results are as follows:

°C	Hard porcelain Vol. weight 2290 kg./m.³ (cal./m. hr. °C)	Kieselguhr brick Vol. weight 400 kg./m.³ (cal./m. hr. °C)
0	1.21	0.077
200	1.31	0.095
400	1.41	0.118
600	1.51	0.146
800	1.61	0.178

L.E.T.

Thermoinsulated lightweight refractories; their properties and service. P. S. Mamykin. *Uralskaya Metallurgiya*, **1938**, No. 3, pp. 34–40.—The characteristics and classification of lightweight refractories, their principal properties, and the singularity of their service are described. B.E.K.

Ticknor columnar checker. Anon. *Glass Ind.*, **19** [9] 335–40 (1938).—The Ticknor columnar checker is built up of two special shapes of silica block and arranged to form a series of vertical columns throughout the checker chamber. The Ticknor block is a rectangular body of silica 5 in. x 5 in. x 3 in. high, having three vertical lugs or fins projecting a distance of 1 in. from each vertical face. The top of each block has four conical protuberances and the bottom has matching indentations serving as dowels and holes to prevent the blocks slipping over each other and to maintain alignment of the blocks in columns. The vertical fins increase the exposed surface area of the block and are effective because the air or gas passes along the vertical groove of the column without hindrance. The outstanding feature of the new construction is its exceptionally long life without replacement or repair under severe conditions of temperature and flux. Under all conditions the material deposited in the columns was cleaned out conveniently and easily, thus preventing clogging almost completely. Furnaces with Ticknor checkers require less draft than those of straight brick construction. For the one installation in which a strict comparison with other types of construction was possible, a fuel saving of between 5 and 10%, on the basis of fuel per ton of glass melted, was noted. Illustrated. E.J.V.

Trends of industrial power plant practice. F. H. Rosencrants. *Combustion*, **9** [10] 31–36 (1938).—An analysis of about four hundred steam generating units indicates a trend toward larger units and higher steam

pressures, bent-tube boilers, and increased use of heat recovery equipment with stokers being about on par with pulverized coal firing. Much of the advancement in industrial power plant practice has been predicated on experience gained in the central station field. R. discusses boiler settings, feedwater conditioning, and steam purification. H.E.S.

SEPARATE PUBLICATION

Cupola refractories. ANON. *Nat. Bur. Standards Simplified Practice Recommendation*, R154-38, 18 pp. Supt. of Documents, Govt. Printing Office, Washington, D. C. Price 10¢. This is a revision of *Simplified Practice Recommendation*, R154-34, which it supersedes. The following items have been added to the original list: 9 sizes of 6-in. cupola blocks for diameters larger than those formerly listed, 20 sizes of 9-in. cupola blocks for outside diameters ranging from 66 to 168 in., and 8 sizes of 4½-in. Colliau blocks for outside diameters ranging from 25 to 82 in. R.A.H.

PATENTS

Bell type annealing furnace. A. V. RITTS AND O. R. OLSON (Pennsylvania Industrial Engineers). U. S. 2,144,742, Jan. 24, 1939 (Aug. 17, 1937). A portable bell type annealing furnace comprises a framework, a refractory bell structure carried by the framework, and a bell-like metal shell inside the refractory bell and also carried by the framework so as to be transportable with the furnace.

Ceramic materials. GEORGES L. DIMITRI. Fr. 826,294, March 28, 1938; *Chem. Abs.*, **32**, 7692 (1938).—Finely divided silicates of Al and (or) Mg are mixed with oils or resins in successive doses separated by intervals of rest. The mixture is brought to the colloidal state, molded, subjected to a pressure of several atmospheres, heated to 100° to 150°, and slowly cooled. The product is afterward fired in known manner.

Fireproof chromite brick. ARTHUR SPRENGER. Ger. 667,691, Oct. 20, 1938 (Jan. 20, 1934); VI/80*b*. 8.04. Fireproof chromite brick consists chiefly of ground chromite ore, which contains FeO and MgO and, as far as possible in equimolecular proportions, Al_2O_3, Cr_2O_3, and Fe_2O_3. The proportions of molecules of Al_2O_3, Cr_2O_3, and Fe_2O_3 to molecules of FeO and MgO is almost equal to 1. The brick contains less than 3% SiO_2, binding or adhesive organic or inorganic materials low in SiO_2, and, if desired, other SiO_2-free materials as admixtures. D.A.B.

Industrial furnace, etc. WILLY LINDER. U. S. 2,146,751, Feb. 14, 1939 (Dec. 17, 1935). A furnace roof for high-temperature industrial furnaces comprises an arched roof formed of individual refractory brick arranged in an arc and suspended to span the furnace side walls freely thereof.

Method and device for producing pure Al_2O_3. A. S. BURMAN. Swiss 199,776, May 26, 1937; *Chem.-Ztg.*, **62** [100] 905 (1938). D.A.B.

Method of manufacture of alumina. J. C. SEAILLES. Brit. 498,569, Jan. 25, 1939 (March 6, 1937).

Preparation of alumina. MONTECATINI SOC. GÉNÉRALE PER L'INDUSTRIA, MINERARIA. ED AGRICOLA. Brit. 498,864, Jan. 25, 1939 (July 20, 1936).

Production of alumina and its derivatives. GEB. GIULINI GES. Brit. 498,510, Jan. 25, 1939 (April 2, 1936).

Production of fireproof products. SOC. ANON. DES MANUFACTURES DES GLACES & PRODUITS CHIMIQUES DE ST.-GOBAIN, CHAUNY & CIREY. Ger. 664,943, Aug. 25, 1938 (Jan. 17, 1935); VI/80*b*. 8.13. Fireproof products are manufactured by sintering a mixture of zirconium silicate and aluminum oxide. The aluminum oxide is added in such an amount that all the silicon dioxide set free by decomposition of the zirconium silicate upon sintering at a temperature over 1500°C is combined as aluminum silicate. D.A.B.

Refractory cast block and method of producing. G. S. FULCHER (Corhart Refractories Co.). U. S. 2,145,113, Jan. 24, 1939 (Dec. 21, 1936).

Refractory vitreous materials. GENERAL ELECTRIC CO., LTD., AND M. PIRANI. Brit. 498,944, Feb. 1, 1939 (Oct. 27, 1937).

Terra Cotta

Ceramic facings: lithoceramics or clinker; tile and mosaic. ANON. *Ceram. & Laterizi*, **1938**, May–Aug., pp. 22–27.—The uses of brick in exteriors to break and vary the frequently monotonous line in modern architecture and artistic effects obtained with tile and mosaic in interiors are illustrated. See "Ceramics—," *Ceram. Abs.*, **18** [3] 78 (1939). M.V.C.

Porcelain instead of metal. P. MARTELL. *Tech. Gemeindeblatt*, **41**, 192–94 (1938); *Chem. Abs.*, **32**, 9420 (1938).—M. discusses the use of porcelain for pipes, pipe fittings, valves, etc.

Stoneware then and now. JOSEF ROBITSCHEK. *Chem. Obzor*, **12**, 257–59 (1937); *Chem. Abs.*, **32**, 9420 (1938).—At the John David Starck plant at Kasnějov (near Pilsen) the chemical composition, porosity, and technical properties of stoneware have changed greatly in the past 100 years but only slightly during the past decade. Recent developments have been in increased density of the shard which, during the past 10 years, has increased the hardness from 550 kg./sq. cm. to 2200 kg./sq. cm. Stoneware is now being manufactured in light even colors and is resistant to large temperature changes and to heating or cooling by liquids which makes it adaptable to the textile industry.

Zinc-vapor glazing of clays: I, Effect of variable iron oxide and alkalis in clays on zinc-vapor glaze colors. C. MAJOR LAMPMAN AND H. G. SCHURECHT. *Jour. Amer. Ceram. Soc.*, **22** [3] 91–95 (1939).

PATENTS

Engobing method for obtaining glazing effects and, at the same time, coloring the upper surfaces of unglazed brick, tile, earthenware, and pottery. I. G. FARBENINDUSTRIE A.-G. Ger. 665,266, Sept. 1, 1938 (May 19, 1934); VI/80*b*. 23.07. The unfired ware is treated with solutions or suspensions containing metallic coloring compounds, phosphoric acid, and, if desired, alkalis (including ammonia) in proportions corresponding to the formula $xMe_1 \cdot yMe_2 \cdot z(PO_4)$, where Me_1 = alkali metal and/or ammonia, Me_2 = the heavy coloring metals, x = not more than 2, y = 1 at the most, and z = the valence of Me_2. The ware is then subjected to an oxidizing firing; after the highest firing temperature is reached, the ware is subjected to a reducing firing for a short time. D.A.B.

Grooved tile. CARL LUDOWICI K. A. A. Ger. 665,166, Sept. 1, 1938 (March 5, 1935); V/37*c*. 1.01. A tile is designed with a grooving to enable overlapping of the tile to make it weather resistant. D.A.B.

Roofing tile, etc. A. GOSDEN. Brit. 498,926, Feb. 1, 1939 (July 19, 1937).

Tile structure. A. H. STEWART. U. S. 2,145,103, Jan. 24, 1939 (Oct. 6, 1936). In an article of manufacture, a tile having a mount element secured to and extending from a back face thereof and a longitudinally extending mount element adapted to be mounted on a building construction, the second-mentioned element having track portions slidably receiving the first-mentioned element.

Whiteware

Ceramic raw materials for dry-plastic working. C. SCHUSTERIUS. *Naturwissenschaften*, **26**, 394–98 (1938); *Brit. Chem. & Phys. Abs.-B*, **57** [10] 1160 (1938).—The use of steatite as a raw material for "pressed" ceramic work is described. The difficulties encountered in using mica for this purpose are mentioned, and the advantages of sericite are described.

Flashover characteristics of (porcelain) insulation. P.

H. McAULEY. *Elec. Jour.*, **35**, 273–80 (1938); *Chem. Abs.*, **32**, 8722 (1938).—A series of 53 curve sheets illustrates the impulse strength of porcelain umbrella insulators exposed to various conditions. The 1.5 × 40 microsecond wave has become an accepted standard in the U. S. The data are valuable in the design and selection of insulators.

High-tension porcelain bushings with sealed-up hollow interior. K. SCHANDINN. *Stemag-Nachr.*, No. 16–17, pp. 499–502 (1938).—S. describes several methods whereby a large type of porcelain transformer bushing with a closed top is supplied with a partly closed bottom section which may be sealed gas tight by a suitable glass. Prior to the sealing operation the bushing is entirely evacuated, and the hollow interior is filled with dried nitrogen gas at atmospheric pressure or at a pressure of approximately 30 lb./sq. in. Illustrated. L.E.T.

Producing cup handles. A. N. POPLAVKO. *Stroitel. Materialy*, **1938**, No. 3, pp. 30–31.—P. describes the construction of a new stamping machine producing 151,200 handles a day. P.B. & E.S.

Sipa bodies. E. ALBERS-SCHÖNBERG. *Stemag-Nachr.*, No. 16–17, pp. 469–75 (1938).—A series of ceramic bodies consisting of a clay substance and talc with small additions of other fluxes is described. They belong to the ternary system MgO–Al_2O_3–SiO_2. A characteristic of these bodies is the exceptionally low coefficient of thermal expansion which varies between 1.1 and 2.0 × 10^{-6} (20°C to 200°C). Sipa 14 has a porosity of 1 to 5%, and the fired color is dark brown; Sipa 11 has a porosity of 15% and has a light brown color; Sipa H is a highly vitrified product. The latter (fired at cone 14) has the lowest thermal expansion and great toughness and is used for high tension insulation and for coils in radio work. Illustrated. See "Ceramic—," *Ceram. Abs.*, **17** [6] 224 (1938). L.E.T.

Talc porcelain: XIV, Thermal expansion of talc porcelain. SEIJI KONDO AND SHIN-ICHI SUZUKI. *Jour. Soc. Chem. Ind. Japan*, **41**, 197B (1938).—The coefficients of thermal expansion of talc porcelains varied from 1.36 to 9.55 × 10^{-6} in the range 0° to 600°. Highly talcose bodies show high expansion and *vice versa*. Highly talcose or highly siliceous bodies are likely to contain cristobalite. Its presence can be avoided by the introduction of small amounts of alkaline earths, mineralizers, or other fluxes, and lower expansion is obtained thereby. The coefficient decreases with decrease in the molecular ratio SiO_2/R_2O_3. At a constant ratio the coefficient is reduced with increase in MgO. Poor thermal durability is associated with high expansion and high cristobalite. **XV, Mechanical strengths of talc porcelain.** *Ibid.*, pp. 197–98B; *Chem. Abs.*, **32**, 8722 (1938).—Absorption and shrinkage increase with increase in the percentage of mixing water between 0 and 8% and with decrease in the pressure between 3000 and 250 kg./sq.cm. If the pressed bodies contain no water, the strengths of the fired specimens increase with increase in pressure. In the presence of water, a maximum is reached at 500 to 750 kg./sq.cm. due to slipping in the bodies. The highest strengths were compression 10,200, modulus of rupture 1153, and impact strength 3.30 cm.-kg./sq. cm. For Part XIII see *Ceram. Abs.*, **18** [1] 27 (1939).

PATENTS

Ceramic materials. CONSOLIDATED SCIENCES, INC. Fr. 827,788, May 3, 1938; *Chem. Abs.*, **32**, 8728 (1938).—The material is composed of MgO 80 to 98% and a slightly acid oxide, *e.g.*, SiO_2, the remainder. The SiO_2 may be added in two stages. Thus, MgO is mixed with 2% of SiO_2 and the mixture is heated to 1400° to 1600°, ground, mixed with 3% SiO_2, molded to the required shape, and heated to vitrification temperature.

Electric insulator. L. A. MEISSE (Ohio Brass Co.). U. S. 2,146,344, Feb. 7, 1939 (Oct. 2, 1937).

Glazing whiteware. WICK-WERKE. Ger. 665,471, Sept. 8, 1938 (April 6, 1936); VI/80*b*. 23.03. Whiteware printed with oil containing coloring matter is dipped into an aqueous glaze and fired in a circular furnace. The printing is dusted over with a mixture of finely ground glass-forming minerals shortly after application of the printing; the article is dipped into the aqueous glaze and finished in a single firing. D.A.B.

Means for supporting pottery, etc., during firing processes. W. E. MADDOCK (John Maddock and Sons, Ltd.). U. S. 2,146,585, Feb. 7, 1939 (Feb. 15, 1937).

Production of vitreous coatings. N. V. PHILIPS' GLOEILAMPENFABRIEKEN. Fr. 827,094, April 15, 1938; *Chem. Abs.*, **32**, 6826 (1938).—A vitreous material, or a mixture of substances from which a vitreous material is obtainable, is converted into a suspension and applied to the surface by electrophoresis. The surface is then heated to convert the layer into a coherent form. The process may be applied, *e.g.*, to the manufacture of coated electrical conductors and electrical condensers. Examples and numerous details are given.

Spark plug. E. R. DARBY (Federal-Mogul Corp.). U. S. 2,146,722, Feb. 14, 1939 (Dec. 16, 1936). GENERAL MOTORS CORP. Brit. 499,259, Feb. 1, 1939 (June 1, 1937). H. L. HALL. Brit. 498,541, Jan. 25, 1939 (Oct. 28, 1937). KARL NITTKA. U. S. 2,144,891, Jan. 24, 1939 (July 25, 1938).

Spark plug having means for automatically varying the spark gap. W. F. KILBURN. Brit. 497,770, Jan. 11, 1939 (Nov. 29, 1937).

Urinal stall. R. H. ZINKIL AND G. R. MCCURDY (Crane Co.). U. S. 2,147,588, Feb. 14, 1939 (Oct. 29, 1936).

Use of porcelain as insulating material for acids possessing piezoelectric properties. HANS NIEDERREITHER. Ger. 665,995, Sept. 22, 1938 (March 31, 1936); IV*b*/12*h*. 1. Porcelain, in the unglazed state and in conjunction with a pliable or elastic underlayer such as a metal, is used as a tight insulating material for acids with piezoelectric properties. D.A.B.

Ventilator for toilet bowls. L. H. PERREAULT. U. S. 2,146,982, Feb. 14, 1939 (March 23, 1938).

Equipment and Apparatus

"Apparent" density of powdered products. F. MARTIN. *Compt. Rend. 17me Congr. Chim. Ind.*, **1937**, pp. 231–35; *Brit. Chem. & Phys. Abs.–B*, **57** [9] 993 (1938).—Bulk volume is a function chiefly of grain shape, texture, and degree of subsidence. From apparent specific volume measurements on inorganic salts and oxides, maximum, minimum, and mean volumes are distinguished and empirically related to yield criteria useful in commercial specification, sampling, and packing.

Application of the Schmidt principle to microscopy. E. H. LINFOOT. *Jour. Sci. Instruments*, **15** [12] 405–406 (1938).—L. describes the methods by which figured Schmidt plates of glass and quartz were constructed for use in microscopes operating on the Schmidt principle. The first microscope, of numerical aperture 0.41, is for visual use; the second, of numerical aperture 0.54, is suited to both visual and ultra-violet microscopy. J.L.G.

Behavior of refractory metals, particularly molybdenum, at high temperatures. New molybdenum electrical resistance furnace. J. MICHEL. *Bull. Acad. Roy. Belgique*, **24**, 333–46 (1938); *Brit. Chem. & Phys. Abs.–B*, **57** [10] 1179 (1938).—The variation of the physical properties of Mo with rise of temperature and under various heat treatments is examined, and loss by volatilization and the action of O_2, N_2, H_2, and impurities from refractories in contact are investigated. A furnace embodying a flat Mo strip (2 x 8 mm.) formed into a helical coil and heated

in an atmosphere of H_2 is described. The rigidity of Mo at high temperature renders support necessary only at the ends.

Birefringence of quartz under compression and its ultraviolet dispersion. G. Bruhat and A. Blanc-Lapierre. *Rev. Optique*, **17**, 137–60 (April, 1938); *Science Abs.-A*, **41** [492] 1142 (1938).—The following cases were investigated: (1) compression parallel to optical axis, propagation of light perpendicular to it; (2) compression perpendicular, propagation parallel to the optical axis; and (3) compression and propogation normal to each other and to the optical axis. In case 2 the birefringence is about 28% less than in cases 1 and 3. In case 3 the effect is independent of the orientation of the pressure in relation to the electric axes. The dispersion agrees with Havelock's formula only to a first approximation. H.K.R.

Color-temperature optical pyrometer. Pyrowerk. *Jour. Sci. Instruments*, **15** [12] 415–18 (1938).—The Bioptix operates on the principle of the difference in color of the heated object at different temperatures. These color differences are assessed by comparison of the relative intensities of radiation of two different wave lengths in the red and green. For all materials which, although deficient in radiating power, are constant in their emissivity factor, this ratio of the intensities is unaffected by departure from black body conditions in taking observations. This method of color measurement, therefore, gives true temperatures for such materials. The filter systems employed are discussed, and the operation of the instrument is described in detail. The range covered is 1000° to 2000°C. The instrument weighs 4 lb. and costs £60. The American agent is the Pyrometer Instrument Co., New York. Illustrated. J.L.G.

Continental advances in the principles, construction, and use of scientific instruments. M. Pirani. *Jour. Sci. Instruments*, **15** [12] 389–405 (1938).—P. gives a review compiled from 43 recent German papers. Specific references are given in each case. The section devoted to the electron microscope is illustrated by three photomicrographs, the largest magnification being taken at 60,000 diameters. J.L.G.

C-SiC thermoelements for measuring high temperatures (to 1800°). V. K. Varsanovich. *Ukrain. Nauch.-Issledovatel Inst., Ogneuporov & Kislotouporov, No 44*, pp. 114–15 (1938).—The C-SiC thermoelement proposed by Fitterer (*Ceram. Abs.*, **16** [1] 32 (1937); **17** [3] 111 (1938)) is recommended for measuring high temperatures in a reducing or carbonizing atmosphere. The thermoelement consists of a tube 20 to 40 mm. in diameter and 1 m. long, closed at one end and of a material suitable to conditions; the inserted bar is put through a porcelain "sleeve" and comes in contact with the tube only in one place, on the base over a difficulty fusible cement; this part of the thermoelement is placed in the temperature zone to be measured, and the water-cooled free end is connected with a galvanometer graduated to 1800°. M.V.C.

Determining the apparent specific gravity of porous and cracked bodies. H. A. Figurovskii. *Zavodskaya Lab.*, **7**, 800–801 (1938).—The device is constructed so that air bubbles observed on the glass walls and on the sample when glass tubes are filled with mercury are eliminated by evacuation. P.B. & E.S.

Developments in clayworking machinery. L. J. Sykes. *Brit. Clayworker*, **47** [561] 315–21 (1939).—S. reviews clayworking machinery in use in the most modern plants, which includes box feeders and proportioners, crushing rolls, extrusion machines, cutting tables, grinding mills, and presses. R.A.H.

Dust counter. Bausch & Lomb Optical Co. *Jour. Sci. Instruments*, **15** [12] 418–19 (1938).—An illuminator is included, and the instrument is airtight so that no chance deposit of dust can occur on the slide under observation. Illustrated. See *Ceram. Abs.*, **16** [3] 94 (1937). J.L.G.

Electrostatic separation: III. Herbert Banks Johnson. *Eng. Mining Jour.*, **139** [12] 41–45 (1938).—J. considers developments in electrostatic separation since 1930. Using a positive charge to repel silica and alumina on Lehigh Valley cement rock, the $CaCO_3$ content was increased at a lower cost than the cost of purer limestone. According to J. there are three types of mineral particles: (1) those repelled with a positive charge and suppressed with a negative charge, (2) those repelled with a negative charge and suppressed with a positive charge, and (3) those unaffected by either polarity. He explains how these factors are used in electrostatic separation of materials formerly thought inseparable by this method. A list of separation voltages and polarities of 90 common minerals is included. Illustrated. For Part II see *Ceram. Abs.*, **18** [2] 55 (1939). J.L.G.

Foundation and development of a supermicroscope. Heinz O. Müller. *Elektrotech. Z.*, **59**, 1189–94 (1938).—M. discusses the light microscope and its limits of resolving power together with the latest developments in the field of electron optics. The construction of a new high-power microscope which permits magnifications and clear pictures up to 28,000× is described. Photomicrographs show the application of this instrument in research on cement (particles magnified 17,800×), clay particles (17,800×), and dust particles (25,500×). L.E.T.

Improved crushing machine saves money. E. H. Fleischman. *Concrete, Cement Mill Ed.*, **47**, 104–105 (1939).—A two-roll crusher has a crushing surface built up by depositing nickel-manganese arc welding rod on it, with one roll preferably corrugated. When worn, more welding rod is deposited. Two hundred pounds of rod, at 80¢/lb. deposited, served for crushing 1,075,000 bbl. of cement clinker from 6 in. to 1 in. or less. The old method of replacing surfaces cost 0.065¢/bbl. while this method costs only 0.015¢/bbl. If used throughout the cement industry, it would save $58,000 per year. W.D.F.

Improvement of drying (by the addition of electrolyte) of small grog products. A. I. Kramarenko. *Zitein-Tech. So.*, Series 27, No. 1041, 2 pp. (1937); abstracted in *Referat. Silikatliteratur*, **5** [4] 5159 (1938).—Tests on Russian refractory clays were made on a laboratory and industrial scale. The electrolyte additions tried were HCl, H_2SO_4, NH_4Cl, NaCl, $CaCl_2$, $Al_2(SO_4)_3$, and $FeSO_4$. $CaCl_2$ was selected as the cheapest by-product from the manufacture of soda. A 0.1 to 0.25 *N* solution of $CaCl_2$ in the water used did not react negatively on the refractoriness and accelerated the drying of three or four clays examined in the laboratory 26 to 30%. In a special apparatus, the presence of (coagulating) $CaCl_2$ prevented the appearance of cracks in the first stage of artificial drying. In a tunnel drier in Chasov-Yar, a 0.025 *N* solution accelerated drying 16%. M.V.C.

Magnetic separators and their possible applications to the beneficiation of Illinois industrial minerals. J. J. Ferris. *Illinois State Geol. Survey Circ.*, No. 23C, pp. 47–54 (1938).—F. reviews the art of magnetic separation and its application in the concentration and beneficiation of a variety of industrial minerals such as coal, gypsum, fluorspar, glass sand, bauxite, clays, zinc and lead ores, silica, etc. He gives the uses of magnetic separators in the ceramic industry for the removal of iron from raw materials such as borax, feldspar, dolomite, and bauxite, from glazes and slips, and from cullet prior to its addition to the batch. F.V.T.

Mechanical disintegration of solids. J. Aumaréchal. *Compt. Rend. 17me Congr. Chim. Ind.*, **1937**, pp. 942–46; *Brit. Chem. & Phys. Abs.-B*, **57** [8] 855 (1938).—Finer grinding than is obtained in existing "colloid" mills can be carried out in a suitably designed and operated roll mill. A. stresses the need for a suitable material of construction and for the attainment of highly finished roll surfaces; the roll pressures should be high. The operating modifications include the adjustment of the relative speeds of the rolls to suit the hardness of the material to be ground and the application to the roll surface of an extremely thin film of some material such as glue without undue cushioning. Careful control of the rate of feed and a suitable means for the removal of the disintegrated material must be provided.

Micropycnometer for the determination of densities of heavy solids. Horace Winchell. *Amer. Mineralogist*, **23** [11] 805–10 (1938).—W. describes a constant volume

quartz-glass pycnometer which in experiments gave results with a probable error of 1%, using 0.03 to 0.04 cc. of material with a specific gravity of 4.0 to 7.5 and weighing on an ordinary chemical balance accurate to 0.0001 g. F.J.Z.

Mixing calorimeter for determining the heat capacity of refractories at high temperatures. Z. E. LOBANOVA. *Zavodskaya Lab.*, **7**, 804–10 (1938).—The bronze-mercury mixing calorimeter enables the direct determination of the heat capacity up to 1000°. A simplified graphical method was worked out to calculate the true heat capacities from medium values. L. suggests a method of calculating heat losses by which it is possible to obtain corrected heat-capacity values independently of their absolute values. A calorimeter of this type can be used for determinations with any material in the form of continuous cones or powders. In the latter case, the samples can be enclosed in capsules of refractory material. P.B. & E.S.

Multiple pantograph and etching apparatus. J. A. HALL. *Jour. Sci. Instruments*, **15** [12] 407–13 (1938).—H. describes the apparatus used at the National Physical Laboratory for etching the mark of approval on the stems of clinical thermometers. It comprises a multiple pantograph capable of marking 36 thermometers at once and semiautomatic machines for applying the HF etch. Illustrated. J.L.G.

Pertinent spray-gun pointers. FRANK V. FAULHABER. *Products Finishing*, **3** [4] 48–50 (1939).—To prove effective, a spray gun, correctly used, should give uniform results with no splitting, dry spots, or dark center and as little mist or overspray as possible. The spray-gun parts should be readily interchangeable so that the spray guns can be procured on short notice and can be inexpensively stocked. The nozzles should be easily and accurately adjustable. The spray gun should not clog too easily and should be durable but must be as mechanically simple as possible. The spray gun should be easily cleaned and should have a minimum of parts contacting with the liquid; these parts should be accessible. The spray operator should have a gun assuring a comfortable grip and proper balance and should be trained to follow the manufacturer's instructions. H.K.R.

Proportioning of materials in process engineering. J. C. WITT. *Concrete, Cement Mill Ed.*, **46**, 265–66, 284–87 (1938).—Proportioning is essential when two or more raw materials are used, and it should be followed by adequate blending. W. gives a procedure for making proportioning calculations quickly and accurately. This is applicable to the proportioning of solids or liquids by weight or volume. In the case where four materials are used to make a product of four components, four equations in four unknowns are needed. A general solution of these equations with literal coefficients is made here. Numerical values are then substituted in the literal solution. This solution may be used for fewer constituents or materials by letting some values be zero. In special cases it can be used for more than four materials. Considerable preliminary information may be obtained from a graph of pounds of materials against pounds of constituents, an example of which is shown. W.D.F.

Relative distribution curve for evaluation of sieve analysis. F. MOGENSEN. *Jernkontorets Ann.*, **122**, 59–83 (1938); *Brit. Chem. & Phys. Abs.-B*, **57** [9] 993 (1938).—The theory of sieving is discussed mathematically. Distribution curves for materials crushed by various methods are given.

Reproduction of daylight for examination of colors. J. PINTE AND R. TOUSSAINT. *Rev. Gén. Mat. Color.*, **42**, 282–84 (1938); *Brit. Chem. & Phys. Abs.-B*, **57** [10] 1112 (1938).—Light of different wave lengths varies greatly in intensity with the source (gray and blue skies, direct sunlight, and incandescent lamps). The importance of reproducing average daylight is discussed, and a suitable lamp employing three dichromatic filters with a single source of light is described.

Sedimentation volume and thixotropy. H. AKANATU. *Bull. Chem. Soc. Japan*, **13** [6] 456–62 (1938).—A. made experiments on the sedimentation volume of powders in liquids. The results show that if the powder is the polar substance the sedimentation volume in the nonpolar liquid is always larger than that in polar liquid; in the case of the nonpolar powder, however, there is no disparity in the sedimentation volume according to the nature of liquid. These results indicate that the selective adsorption and the molecular orientation take place on the surface of the powder. A. found the parallelism between the sedimentation volume and the thixotropic nature of the system as well as some new examples of thixotropic systems. Y.K.

Separation of minerals according to their specific gravity by centrifugalizing in heavy liquids. V. N. DOMINIKOVSKII. *Razvedka Nedr.*, **8** [4–5] 44–49 (1938); abstracted in *Chem. Zentr.*, **1938, II**, 3428.—Heavy liquids, *e.g.*, "tule," density 2.8 to 3.1, were used for centrifugalizing minerals; the following mixture was also used: $CHBr_3$—alcohol, $CHBr_3$—toluene, $CHBr_3$—oil, and CH_3I—toluene. The grain size of the minerals is decisive for centrifugalizing, as, if it is irregular, errors can not be avoided. The liquid mixture given above can be separated by freezing out. M.V.C.

Standardization of a scale of color temperatures. H. DJOUDAT. *Rev. Optique*, **16**, 401–22 (1937); *Jour. Soc. Glass Tech.*, **22** [92] A280 (1938).—The color temperatures of a carbon filament lamp between 1900° and 2100°K, two tungsten filament vacuum lamps between 2000° and 2360°K, and two gas-filled tungsten filament lamps between 2300° and 2800°K were measured by photometric comparison with a black body radiating at the same temperature as the lamps or lower. Tables and equations are given relating the color temperature of the lamp to its applied voltage and filament current for all the lamps examined. These equations are all of the form, color temperature $T = a + b \cdot I = c + d \cdot \sqrt{V}$, where I = the filament current, V = the applied voltage, and a, b, c, and d = constants depending on the characteristics of the lamps. The maximum error in a single measurement of the color temperature of a lamp is estimated to be 11°, and that of a mean of 25 measurements, less than 5°.

Substitute for the quartz wedge used with the polarizing microscope. C. D. WEST. *Amer. Mineralogist*, **23** [8] 531–33 (1938). F.J.Z.

Sulfur cores; their use in the manufacture of molds for fine ceramics. PIERRE RENAULT. *Céram., Verrerie, Email.*, **6** [10] 285–92; [11] 325–31 (1938).—The use of sulfur cores for fine ceramic molds gives excellent results and is easy when precautions are observed. Sulfur cores are superior to plaster cores: they are much harder and there is much less breakage in the molding of very delicate pieces, such as handles for cups. They reproduce details of relief, ornament, and engraving with greater sharpness and are little affected by the expansion of the plaster during setting. They are easily removed without causing flaws. The use of sulfur cores is restricted, however, by the sensitivity of sulfur to shock; when damaged, they can not be repaired. R. gives the properties and organoleptic character of sulfur and describes the preparation, fusion, and casting of molds. M.V.C.

Vision through optical instruments. T. SMITH. *Proc. Phys. Soc.* [London], **50** [6] 863–88 (1938).—S. deals with the various phases of optics. A number of diagrams is presented. L.E.T.

Visual examination of moving fans. M. CHAPPUIS. *Chaleur & Ind.*, **19** [221] 505–11 (1938).—On the premise that, for small pressure gradients existing in blower systems, air behaves as an incompressible fluid, C. studied the motion of small particles suspended in water which was fed through centrifugal fans at a velocity one-tenth that of the service air velocity to compensate for the viscosity difference. Eight- and sixteen-blade fans were studied with the aid of moving cameras. "Dead" zones were discovered, indicating inefficiency in fan design. V.D.F.

Zirconium and its compounds with a high melting point. J. D. FAST. *Phillips Tech. Rev.*, **3** [12] 345–52 (1938).—F. describes the preparation and mechanical, electrical, and chemical properties of zirconium metal. The melting points of its compounds are as follows: Zr 1860°, ZrO_2 2700°, ZrN 2980°, and ZrC 3530°. The use of ZrO_2 in

the manufacture of refractory articles for use above 2000°C is noted. If pure ZrO_2 is used, cracks develop due to a change of structure at 1000°C which causes a 7% contraction in volume. Adding a few percent MgO and heating above 1700°C prevents this; 2% MgO plus 0.5% BeO is better than MgO alone. A mixture of four parts TaC plus one part ZrC has the highest melting point of any known substance, about 4000°C. H.K.R.

PATENTS

Apparatus for electrically testing the thickness of coatings. W. H. TAIT. Brit. 498,032, Jan. 18, 1939 (March 25, 1937).

Apparatus for purifying or dressing clay. L. GERECHT. Brit. 499,100, Feb. 1, 1939 (May 4, 1937).

Apparatus for surface treatment of green clay. E. B. JONES. U. S. 2,146,957, Feb. 14, 1939 (July 6, 1937). Apparatus for the surface treatment before firing of green clay, shale, etc., products such as brick.

Brickmaking machine. T. C. FAWCETT, LTD., D. L. FAWCETT, AND A. E. BOTTOMLEY. Brit. 498,189, Jan. 18, 1939 (Oct. 5, 1937).

Clay gun. H. A. BRASSERT & CO., LTD., AND J. MILES. Brit. 498,446, Jan. 18, 1939 (March 1, 1938).

Concentrating minerals from their ores. PHOSPHATE RECOVERY CORP. Brit. 498,450, Jan. 18, 1939 (April 27, 1937).

Deaired wire cutting press for ceramic charges. GÜTTLER & COMP. MASCHINENFABRIK. Ger. 667,579, Oct. 20, 1938 (July 10, 1934); VI/80*a*. 26. Ceramic charges are mixed in a mixing trough by means of wheels with blades, and the charge is moved by screw wheels through a slit-like opening into a press cylinder. D.A.B.

Disintegrating elements for machines deairing clay masses. OTTO MANFRED (Eisen- und Hartgusswerk Concordia G.m.b.H.). Ger. 667,825, Oct. 27, 1938 (Oct. 5, 1936); VI/80*a*. 26. The elements consist of two plates with slots and are so arranged that one plate is placed over the other and the slots cross each other. The crosspieces of the lower plate are more knifelike and thinner than those of the upper plate. D.A.B.

Heating conductors for electric furnaces. N. V. MOLYBDENUM CO. Brit. 499,623, Feb. 8, 1939 (July 22, 1937).

Heating furnaces for melting glass, silicates, and other refractory material. GEORG ZOTOS. U. S. 2,147,476, Feb. 14, 1939 (Feb. 9, 1937). A method of heating a high-temperature rapidly revolving tube furnace for melting glass, silicates, and other refractory material by combustion of a fuel by means of oxygen consists in that the highly superheated waste gas due to combustion is regenerated immediately after its exit from the furnace by means of a reducing substance and that at least part of the regenerated waste gas is directed in continuous circulation into the furnace.

Horizontal press, clay cutter, and clay mixer with device for degassing moist clays. RICHARD RAUPACH MASCHINENFABRIK GÖRLITZ G.M.B.H. Ger. 666,179, Sept. 22, 1938 (Nov. 8, 1935); VI/80*a*. 26. The first worm screw inside of the degassing chamber consists of single thin cutting knives. The propelling surface of each cutting knife is so narrow that the degassed mass does not adhere; the number of knives compensates their width and thus maintains the propelling or pushing force. D.A.B.

Improving the strength and abrasive properties of iron. A. CROFT. Brit. 499,647, Feb. 8, 1939 (July 21, 1937).

Making ceramic ware. F. G. MONTGOMERY (Ekstrand Mfg. Co.). U. S. 2,146,309, Feb. 7, 1939 (Jan. 7, 1938). The process of forming intaglio colored effects in ceramic ware consists in molding the ware to provide a raised mass in a portion thereof and imprinting therein a character such as an insignia, coating the ware with a material of a color different from that of the color of the basic ceramic material, removing the coating from the top surface of the mass before it hardens to expose the color of the basic material and expose a plane surface to view in which the character appears in intaglio effect.

Method and apparatus for producing refractories. H. K. RIGDON. U. S. 2,144,852, Jan. 24, 1939 (Feb. 12, 1938). An apparatus for cutting a column of plastic material into sections while the column is being emitted from an extruding machine comprises a tool support, means sustaining it for rotation about the column substantially on the longitudinal axis thereof and for reciprocation along the column, a tool reciprocably carried by the support in a position to penetrate the column substantially radially thereof, means reciprocating the tool support and causing it to travel in one direction with and at the same speed as the column, means for rotating the tool support, and means for projecting the tool into the column substantially radially thereof while the tool support is moving in the aforesaid direction and for effecting retraction of the tool before the support moves in the opposite direction.

Process and apparatus for vaporizing or gasifying metals, metal alloys, metal compounds, and other solid mineral substances difficult to vaporize. R. MAIER. Brit. 498,-921, Feb. 1, 1939 (June 8, 1936).

Spray-gun nozzle. SVEND BRAMSEN AND F. W. WAHLIN (Binks Mfg. Co.). U. S. 2,146,416, Feb. 7, 1939 (Oct. 31, 1935; Nov. 8, 1937).

Stenciling apparatus. T. H. SLOAN (Simplex Engineering Co.). U. S. 2,146,773, Feb. 14, 1939 (July 10, 1936; renewed May 12, 1938).

Surface decorating machine. C. A. WULF. U. S. 2,146,411, Feb. 7, 1939 (Oct. 2, 1936).

Tile cutting gage. S. J. ZANGRANDO. U. S. 2,144,697, Jan. 24, 1939 (April 21, 1938).

Kilns, Furnaces, Fuels, and Combustion

Bringing insulation facts up to date. G. E. GRIMSHAW. *Heat Treating & Forging*, **25** [1] 40–43 (1939).—G. considers the properties of eleven insulating materials for industrial ovens operating at 200° to 1000°F and gives the conductivities, heat capacities, allowable temperatures, and weights. Economical thickness of insulation is determined by minimum total annual costs (cost of insulation plus fuel costs). Other factors sometimes influence this choice. S.S.

Combustion of pulverized coal. H. KREISINGER. *Combustion*, **9** [7] 23–28 (1938).—K. discusses the effect of various factors on the ignition and follows the process of combustion through the furnace. The factors considered are the amount of primary air, admission of secondary air, fineness of coal, the percentage of moisture and volatile matter in coal, characteristics of the ash, mixing, oxygen concentration, and the furnace temperature. Nothing is gained by going to a temperature beyond that required for quick ignition. H.E.S.

Design and firing of kilns: XII, Modern practice. ANON. *Brit. Clayworker*, **47** [561] 305–306 (1939).—Technical developments in the Hoffman continuous kiln in recent years are reviewed. For Parts **X–XI** see *Ceram. Abs.*, **18** [3] 82 (1939). R.A.H.

Equations and quadrant charts for determining heat balances of kilns using solid or liquid fuels. KENNETH G. SKINNER. *Jour. Amer. Ceram. Soc.*, **22** [3] 72–82 (1939); see *ibid.*, **20** [4] 99–111 (1937).

General survey of fuels and furnaces during 1938. EMIL VIEROW. *Heat Treating & Forging*, **25** [1] 35–37 (1939).—Steel plant fuel costs have been reduced by proper allocation of various fuels to different operations and by the application of blast-furnace gas mixed with coke-oven gas or purchased gas or oil to metallurgical operations. Blast-furnace gas can be used to maintain temperature during standby or periods of light load. Further recuperation gives the necessary heat when using this leaner gas. Open-hearth and ingot-heating furnaces have improved in firing

port design, regenerator operation, insulation, and temperature control. The use of radiant tube special atmosphere furnaces for annealing and heat treating has been further extended. There has been a wider use of convection, immersion, and submersion heating equipment for miscellaneous purposes. S.S.

Heat transfer in revolving reverberatory furnaces. A. ROMWALTER, JR. *Magyar Kir. József Nádor Müszaki és Gazdaságtudományi Egyetem Bánya-, Kohó-és Erdömérnöki Kar, Sopron. A bánya és kohómérnöki osztály Közleményei*, **10** [Part 1] 301–309 (1938).—Heat transfer from the flame to the charge by convection and radiation is investigated. The heat transfer can be increased by using a lining of good heat conductivity which at the same time increases the life of the furnace. Practical examples are given. M.H.

Influence of particle size in processes of fuel technology. P. O. ROSIN. *Trans. Inst. Chem. Engrs.* [Preprint], 20 pp. (Oct., 1937).—R. attempts to state comprehensively the principal factors affecting the influence of particle size in fuel technology. A.B.S.

Measuring accurately the temperature of a flowing gas. ANON. *Glass Ind.*, **19** [11] 423–24 (1938).—The usual method of inserting a thermometer or thermocouple into a gas stream may give an erroneous reading because the flow of heat by radiation between the measuring device and its surroundings radically affects the indicated temperature. The apparent temperature may be brought closer to the true temperature if the rate of heat transfer by conduction is increased. This may be accomplished by using a couple made of very small wire with a small bead at the junction. By far the most satisfactory method yet devised for accurately measuring the temperatures of flowing gases is the use of the high velocity or suction thermocouple. E.J.V.

Minimizing coal segregation. H. V. SCHIEFER. *Combustion*, **9** [9] 36–37 (1938).—S. discusses methods by which segregation of coal can be controlled through the employment of a cylindrical bunker and weigh larry. H.E.S.

Monolithic floor of tunnel kiln car for brick plants. E. A. GERMAN. *Stroitel. Materialy*, **1938**, No. 4, pp. 23–29.—A car lined with a concrete mass based on aluminous cement can make over 24 runs without repairs as compared with 1 run in the case of a brick lining. The repairs on a refractory concrete lining can be made by pouring the same mass over the damaged places. P.B. & E.S.

Pulverized wood fuel for pottery firing. S. ISIZUKA. *Jour. Fuel Soc. Japan*, **17** [194] 1159–71 (1938).—In Japan, wood is widely used as a fuel in the pottery industry. It has a low sulfur content and the flame is long and mellow, but the calorific value is low; fresh wood and sawdust contain as much as 40% moisture, making it necessary to dry it to increase the heating value. The heating values of sawdust are 4231 cal. for 22.5% moisture, 4709 cal. when dried at 75°C for 1 hr., and 4736 cal. when dried to constant weight. I. describes a method of firing pottery by using pulverized wood or sawdust together with compressed air. A small rotary drier was used. The drying temperature is about 400°C at the inlet and 200°C at the outlet. The capacity is 180 kg./hr., and the moisture of the fuel decreases from 40% to 10%. The results of the firing tests on the pottery kilns are reported. Comparison is made with other fuels, such as coal, pine, oil, and electrical heat. Results show that pulverized wood gives a big saving in fuel, as the entrance of excess air is prevented to a great extent. Y.K.

SEPARATE PUBLICATIONS

Coke from Illinois coals. GILBERT THIESSEN, W. H. VOSKUIL, AND PAUL E. GROTTS. *Illinois State Geol. Survey Bull.*, No. 64, 235 pp. (1937). F.V.T.

Competitive position of Illinois coal in the Illinois coal market area. WALTER H. VOSKUIL. *Illinois State Geol. Survey Bull.*, No. 63, 110 pp. (1936).—V. presents a detailed analysis of the nature and extent of the competition from other sources of energy with a view to evaluating the economic position and outlook for the Illinois coal industry. The scope includes an analysis of the energy contribution of fuel oil, natural gas, coal from outside fields, and water power, as well as the quantity of coal supplied by Illinois. The basic unit of comparison employed is the ton of coal. Inclusion of data on trends of consumption of each of the fuels over a number of years facilitates acquaintance with changes in the competitive situation and allows probable future trends to be more critically analyzed. F.V.T.

PATENT

Method and means for stoking continuous kilns. J. PROCTER AND E. PROCTER. Brit. 499,476, Feb. 8, 1939 (Sept. 1, 1938).

Geology

Accurate method for the determination of the components of a heterogeneous particulate mineral system. F. H. GOLDMAN. *Amer. Mineralogist*, **24** [1] 40–41 (1939).—The results obtained show (1) how the shape factor for a mineral may be obtained, (2) how the size distribution curve can be plotted, and (3) how, with this data, the percentage by weight of any constituent may be determined by making a count of the number of particles present. The method is applicable to all powders and rock dusts provided that they have a uniform distribution and that they are large enough to be counted and identified. F.J.Z.

Action of hydrogen peroxide on weathered mica. M. DROSDOFF AND E. F. MILES. *Soil Sci.*, **46** [5] 391–95 (1938).—The exfoliation of weathered mica when treated with H_2O_2 was caused by MnO_2 between the plates. This may provide a simple means of separating the mica from other minerals with which it occurs. G.R.S.

Adsorptive clays of the Texas Gulf Coast. ARTHUR F. HAGNER. *Amer. Mineralogist*, **24** [2] 67–108 (1939).—Numerous clay pits containing an abundance of material suitable for the clarification and purification of petroleum products are operated along the Texas Gulf coastal plain. Much of the original material has altered sufficiently to form adsorptive clay of usable quality. Optical, chemical, and X-ray studies indicate that the principal mineral constituent of the clays as mined is montmorillonite. Microscopic textures and structures, when well preserved, are significant of origin. Many beds represent the result of alteration *in situ* of volcanic ash. Substantial amounts of kaolinite, halloysite, and allophane, however, occur in some deposits. In certain deposits, alteration has been so complete as to obliterate direct evidence of the origin of the clay. The waxy character of many moist clay layers is a convenient indicator in the field. Laboratory study shows that the waxy clays contain more nearly pure montmorillonite than other types which are soft, granular, and kaolinitic. The luster may be attributed to unusual hydration characteristics of montmorillonite. Kaolinitic mixtures occur in the northeastern part of the clay belt, whereas the more nearly pure montmorillonite occurs in the southwestern part. A review of the literature, correlated with field observations, indicates that the fuller's earths of eastern Texas formed during the Eocene and the Oligocene or Miocene epochs. Correlation of the physical, chemical, and optical properties with adsorptive capacity has been attempted. The influence of mineralogical features on adsorptive capacity may be summarized as follows: (*a*) impurities lower adsorptive capacity; (*b*) microscopic structures and textures are apparently not related to adsorptive efficiency; (*c*) the montmorillonite lattice structure permits high adsorption; (*d*) the amount and degree of alteration of original material to clay materially affect adsorptive capacity; (*e*) origin by transportation of clay introduces granular impurities and lowers adsorptive capacity; (*f*) high percentage of removable bases and wa-

ter seems to accompany high adsorptive capacity; (g) montmorillonite is the most highly adsorptive clay mineral studied. F.J.Z.

Alunite: III. Y. Asada. *Bull. Inst. Phys. Chem. Research*, **17**, 178–85 (1938).—A. determined the vapor pressure of crystalline water of alunite and its heat of decomposition. The relation between its vapor pressure and temperature and its rate of decomposition are studied. The heat required for dehydration was 8.5 cal./g. Y.K.

Bauxite deposits. Anon. *Aluminium*, **20** [12] 903–905 (1938).—Deposits in Greece, Australia, France, Holland, India, Italy, Japan, and the U. S. and their quantities, production, and organization are described. A bibliography is given. M.H.

Behavior of calcium, magnesium, and potassium sulfates as influenced by limestone and by dolomite. A lysimeter study. W. H. MacIntire, W. M. Shaw, J. B. Young, and Brooks Robinson. *Soil Sci.*, **46** [3] 229–47 (1938).—A 7-year lysimeter study was conducted with a brown silty clay loam to determine the fate of equivalent annual additions of SO_4 in combinations with Ca, Mg, and K and interchange between those cations, with and without single initial supplements of limestone and dolomite. 24 references. G.R.S.

Brookite crystals in the Dogger. R. H. Rastall. *Geol. Mag.*, **75**, 433–40 (1938).—Brookite is widely distributed as a heavy mineral in several different kinds of sediments in the Yorkshire Jurassic. There are two common varieties, one forming plates parallel to the front pinacoid and the other forming plates parallel to the base. Several other varieties characterized by differently elongated plates, an hourglass structure, and very small dispersion are found. Part of these crystals grew in place and part were derived from other sources. W.D.F.

Cambridge collection of rock slices. Alfred Harker. *Geol. Mag.*, **76**, 35–37 (1939).—This collection started sixty years ago and has grown by donation, purchase, and manufacture to 40,000 slices. W.D.F.

Ceramic interests in the Division of Geology and Geography, National Research Council. Robert B. Sosman. *Bull. Amer. Ceram. Soc.*, **18** [2] 76–77 (1939); see *ibid.*, **16** [6] 249–50 (1937).

Classification of igneous rocks: historical approach. S. I. Tomkeieff. *Geol. Mag.*, **76**, 41–48 (1939).—Igneous rocks have been classified according to one or more of the following factors: (1) mineral composition, (2) chemical composition, (3) texture, (4) mode of origin, (5) mode of occurrence, (6) age, and (7) areal distribution. The petrographical classification should be based on the first three, leaving the others to a geological classification. All previous attempts to produce a unified classification based on both these aspects, the petrographical and the geological, have failed. W.D.F.

Composition and occurrence of garnets. W. I. Wright. *Amer. Mineralogist*, **23** [7] 436–45 (1938).—W. shows the constancy of one variety of garnet in each type of rock and demonstrates that the recognition of the rock type is an important aid in determining the chemical composition of garnets by physical methods. F.J.Z.

Conquest of the Dead Sea. Harold G. Shepstone. *Sci. Amer.*, **160**, 10–12 (1939).—At a plant recently built, the water is pumped out and allowed to flow through 1200 acres of evaporating pans, where common salt and carnallite are separated. Liquid bromine is obtained in the bromine factory from the remaining brine; further evaporation produces magnesium chloride. Pure potassium chloride is produced from the carnallite. Present production is 30,000 tons of potash and 1200 tons of bromine a year. Reserves are over a billion tons of potash and nearly as much bromine. The Jordan river adds 40,000 tons of potash yearly. W.D.F.

Constitution of steatite: I, Crystalline phase. Wilhelm Büssem and Carl Schusterius. *Wiss. Veröffent. Siemens-Werken*, **17** [1] 59–77 (1938).—On heating to 800°, talc lost its H_2O and was transformed into protoenstatite (I). On heating to higher temperature, I went over into clinoenstatite (II), appreciably, however, only at a temperature of 1400° or above. The phases were identified by X-ray examination of heated thin sections according to the method of Brentane. If powder photographs were taken, only II was observed at all temperatures. This was due to the conversion of unstable I into stable II by mechanical pulverization of the heated samples. On heating MgO with quartz, forsterite was formed at 1200°, while I began to appear at 1400°. If the samples were pulverized, II tended to appear in place of I. The formation of II was also promoted by the use of hydrated SiO_2 in place of quartz and by the presence of mineralizers such as Li_2O, fluorspar, H_3BO_3, and borax. Steatite gave rise on heating to I, but at 1300° II began to appear. Masses of heated talc, etc., consisting of I, broke down on standing because of transformation of I to II. The rate of transformation appeared to be promoted by large grain size and by the presence of mineralizing impurities and was retarded by the presence of glass. II is the stable phase at all temperatures, I is unstable, and enstatite is uncertain. **II, Glass phase.** Wilhelm Büssem, Carl Schusterius, and Karl Stuckardt. *Ibid.*, pp. 77–89; *Chem. Abs.*, **32**, 5337 (1938).—The amount of glass phase present on the heating of steatite was estimated by comparing the expected amount of cristobalite and $MgO \cdot SiO_2$, based on phase-rule considerations, with the amount determined from X-ray examination and thermal-expansion curves. Glass (23%) was estimated for a mixture of 82% talc, 14% kaolin, and 4% calcite heated 4 hr. at 1360°. The presence of glass was proved directly by the fluorescence of this mixture when heated with added UO_2. The latter disseminates in the presence of glass. No fluorescence was given by heated talc plus UO_2. 31 references.

Construction of models illustrating the arrangement and packing of atoms in crystals. M. J. Buerger and Robert D. Butler. *Amer. Mineralogist*, **23** [8] 471–512 (1938). F.J.Z.

Cryolite, an important auxiliary material for aluminum manufacture. H. Tuxen. *Aluminium*, **20** [12] 839–44 (1938).—There is practically only one important deposit of cryolite worth mining, *i.e.*, in Ivigtut in southwest Greenland. Cryolite is a monocline crystal, Na_3AlF_6, with specific gravity 2.977, hardness 2.5, and a low refractive index, 1.339. It melts at 1000°C. Geographical and geological conditions of the occurrence are described in detail and a diagram of the treatment from mining to the final products used in enameling and Al production is given. In 1937, 53,000 tons were produced. Because of its monopoly, an attempt was made to produce synthetic cryolite (usually of the composition $3NaF \cdot AlF_3$ but sometimes chiolite, $1.5NaF \cdot AlF_3$). Artificial cryolites, however, are not quite as stable as the natural mineral. M.H.

Crystal structure of vermiculites and mixed vermiculite-chlorites. Sterling B. Hendricks and Merrill E. Jefferson. *Amer. Mineralogist*, **23** [12] 851–62 (1938).—The crystal structure of vermiculite has been determined by the use of X-ray diffraction data from single crystals. Vermiculites have the same type of shifts in the *a* direction as is found in muscovite, talc, and pyrophyllite. They resemble the last two minerals and dickite in having a partially random superposition of structural layers along the *b* axis. Many of the minerals previously described as vermiculites are mixed vermiculite-chlorites similar to the mixed vermiculite-micas described by Gruner. F.J.Z.

Curves of the linear thermal expansion of unfired ceramic materials. V. Bodin and P. Gaillard. *Bull. Inst. Céramique Française*, No. 9 (Jan., 1937); abstracted in *Referat. Silikatliteratur*, **4** [6] 4142 (1937).—Examination of 56 materials shows that (1) the greatest variation is observed in values of the maximum of expansion which lie between 0.04% for clay from Sezamk and 1.54% for a silica mix; (2) shrinkage begins between 475° (clay from Tonkin) and 900°C (clay from Laneais); (3) unfired material has a greater thermal expansion than fired material, due to the fact that expansion of unfired materials is assisted or aided by gas development; (4) shrinkage begins only when the greatest part of H_2O and CO_2 is ex-

pelled from the materials; and (5) pure clays and kaolins lose "water of constitution" between 400° and 500°C. See "Linear—," *Ceram. Abs.*, **17** [7] 260 (1938). M.V.C.

Diaspore clay cast of fossil wood in a Missouri diaspore pit. W. D. KELLER. *Amer. Mineralogist*, **23** [7] 461–63 (1938).—K. describes a specimen of petrified wood found in a diaspore clay pit. F.J.Z.

Evolution of the Criffell-Dalbeattie quartz diorite. Granitization. MALCOLM MACGREGOR. *Geol. Mag.*, **75**, 481–96 (1938).—The two processes involved are metasomatism, caused by permeating magmatic emanations, and the mechanical mixing of this product with the parent magma. Three varieties of sediments (poorly calcareous shales, calcareous shales, and graywackes) were analyzed at several different stages of metamorphism. The results are plotted by three different methods, each showing the converging of the analyses to a quartz diorite. Calculation also showed the parent magma to have an alkali feldspar composition. W.D.F.

Feldspar industry makes new yearly record in 1936. ANON. *Nat. Glass Budget*, **52** [10] 7 (1937).—The feldspar industry in 1936 produced more feldspar than in any year, the sales of crude feldspar surpassing the 1928 peak by 16%. The output of crude feldspar totaled 244,726 long tons valued at $1,303,090. Thirty merchant feldspar mills operating in 14 states sold 236,890 short tons of ground feldspar valued at $3,154,853. H.E.S.

Flint clays of Ural. P. N. PERMIAKOV. *Uralskaya Metallurgiya*, **1938**, No. 9, pp. 28–30.—P. studied the properties of flint clays of a new Ural layer. The depth of this clay occurrence is about 2 to 3 m. from the surface of the earth. B.E.K.

Formation of structure in soil: V, Granular structure. D. I. SIDERI. *Soil Sci.*, **46** [3] 267–71 (1938).—The interpretation of the form of the structural elements of chernozem soils can be based on the study of the decomposition of the complex mixed sand-clay-humus formations. The form of the typical granular structure of chernozem is a sign of the accumulation of amorphous humus at the periphery of the aggregate. Increase of the exchange capacity of soil must be closely connected with the appearance of amorphous humus at the periphery of the aggregate. If organic matter is firmly bound with clay as an anisotropic formation, no marked increase in the adsorption capacity occurs. **VI, Microscopic investigation of soil structure in reflected light.** *Ibid.*, [4] 337–49.—The method proved very sensitive in observations on structure changes; it can be used as a control and for purposes of comparison with other methods of soil structure analysis. For Part IV see *Ceram. Abs.*, **18** [1] 33 (1939). G.R.S.

Geology of the Lizard peninsula: I, Mullion rocks. J. B. SCRIVENOR. *Geol. Mag.*, **75**, 304–308 (1938).—Veins showing flow structure and containing orthoclase, albite, biotite, garnet, and tourmaline are found in Mullion Cove. These veins could not be derived from the same source as the Kennack gneiss, as previously believed. South of Mullion Harbor is a lenticle in serpentine, a decomposed remnant of a dolerite dike, containing pyroxene, chlorite, prehnite, sphene, garnet, and opaque material. **II, Primary hornblende schists and gneisses.** *Ibid.*, pp. 385–94.—These are primary and not metamorphic and at the contact were injected *lit-par-lit* into the older rocks. **III, Epidote bands, lenticles, and veins.** *Ibid.*, pp. 515–26.—Rocks very rich in epidote occur as bands and lenticles parallel to the foliation of the hornblende schist and older schists; in some places they cut them as veins. Possibly they result from the complete assimilation of a calcareous rock. **IV, "Devil's Frying Pan," Cadgwith.** *Ibid.*, **76**, 37–41 (1939).—Here the serpentine was intruded into the hornblende schist while the latter was still hot. The Kennack gneiss intruded the serpentine. See "Anthophyllite—," *Ceram. Abs.*, **17** [3] 114 (1938). W.D.F.

Graphic method of determining the optic sign and true axial angle from refractive indices of biaxial minerals. J. H. LANE, JR., AND H. T. U. SMITH. *Amer. Mineralogist*, **23** [7] 457–60 (1938). F.J.Z.

Ground movement and subsidence studies in mining coal, ores, and nonmetallic minerals. GEORGE S. RICE. *Amer. Inst. Mining Met. Engrs. Tech. Pub.*, No. 1014; *Mining Tech.*, **3** [1] 15 pp. (1939).—R. reviews fifteen years' work done by the Ground Movement and Subsidence Committee. W.D.F.

Hydrothermal formation of clay minerals in the laboratory. F. H. NORTON. *Amer. Mineralogist*, **24** [1] 1–17 (1939).—N. exposed a number of feldspars and other aluminosilicates to CO_2-charged percolating water under high pressures and temperatures in a reaction chamber. A study of the end products indicated that the least stable of these materials readily broke down to form clay minerals, the greatest reaction rate occurring at 300°C and a maximum CO_2 pressure. The parent minerals were stable at temperatures outside the range of 250° to 350°C. The production of clay minerals similar to, if not identical with, kaolinite, beidellite, sericite, pyrophyllite, and gibbsite was accomplished. The resulting end product seems to be determined by the nature of the parent rock as well as by the temperature and acidity during the reaction. F.J.Z.

Igneous rocks from the Abercorn and Kasama districts, Northern Rhodesia. T. DEANS. *Geol. Mag.*, **75**, 547–58 (1938).—Dominating the geology at the headwaters of the Zambezi River, one source of the Congo, are the Kundelungu sedimentaries, arkose, sandstone, quartzite, and shale, resting unconformably on a granite floor. The granite intrudes a basement complex of schists, etc., and a series of phyllites and hornfels and metamorphoses a porphyrite series. A system of giant quartz veins, up to 1/4 mile wide for a single vein, cuts all the formations. W.D.F.

Inesite. JEWELL J. GLASS AND WALDEMAR T. SCHALLER. *Amer. Mineralogist*, **24** [1] 26–39 (1939).—Inesite, a hydrous manganese calcium silicate, was analyzed and its properties were determined. Calcium is present in a fixed quantity and does not vary reciprocally with manganese as it does in rhodonite. The most probable formula is the complex one, $15SiO_2 \cdot 3CaO \cdot 11MnO \cdot 10H_2O$. F.J.Z.

Influence of environmental factors on numbers of soil microörganisms. W. G. E. EGGLETON. *Soil Sci.*, **46** [5] 351–63 (1938).—Within the limits studied, soil temperature and soil reaction appeared to exert no measurable influence on numbers of organisms. G.R.S.

Influence of salts and soil-water ratio on p_H value of soils. AMAR NATH PURI AND A. G. ASGHAR. *Soil Sci.*, **46** [3] 249–57 (1938).—The effect of salts and soil-water ratio on soil reaction was studied. The salts have a profound influence on soil reaction, which alters appreciably in the presence of even small quantities of neutral salts. The effect of soil-water ratio on soil reaction is indicated in so far as the soil water alters the concentration of the salts present. In the absence of salts the p_H value is not affected by soil-water ratio. Since natural soils contain varying amounts of salts, uniformity of results can be obtained only by determining the soil reaction in *N* KCl solution. G.R.S.

Interaction between carbonates and soils. AMAR NATH PURI AND M. I. PURI. *Soil Sci.*, **46** [5] 401–408 (1938).—Soil acidoids and single-base soils behave like true acids and salts, respectively, in their reaction with carbonates of alkali and alkaline earths. G.R.S.

Literature on Italian kaolins and clays. ENNIO CURZI. *Ceram. & Laterisi*, **1938**, Jan.–April, pp. X–XII; May-Aug., pp. XXV–XL.—C. presents a compilation of abstracts of historical writings and all recent articles on Italian kaolins and clays. M.V.C.

Magnesite deposits of Ostmark (Austria). ANON. *Chem.-Ztg.*, **63** [3] 30–32 (1939).—A review of the magnesite industry in Germany's newly annexed Austrain territory is given. The properties of crystalline and amorphous magnesite and its industrial application to fireproof refractory brick are discussed. The processes are illustrated. D.A.B.

Magnesite in South Africa. W. E. SINCLAIR. *Mining Mag.*, **60**, 9–12 (1939).—This deposit is in eastern Trans-

vaal ten miles east of Kaapmuiden and near a railroad. It occurs very irregularly in serpentines and talc schists, sometimes being in thick veins. Adit mining and open quarrying are both used. Selective mining and sorting give a high quality product, analyzing 97% $MgCO_3$. Production is about 1800 tons per year; some is calcined and some is shipped raw. Practically none is exported. Reserves appear to be large. W.D.F.

Mineral fluorescence. EDWARD C. SMITH AND WILLIAM H. PARSONS. *Amer. Mineralogist*, **23** [8] 513–21 (1938).—The availability of an unusual instrument giving monochromatic radiant energy of a higher order of magnitude than hitherto possible permitted this research. Specimens of forty-three minerals representing twenty-one distinct species were examined in ultra-violet radiation, and a tentative relationship between the frequency of the incident radiation and the frequency of the reradiated light was determined. F.J.Z.

Mineral waste reduced. PAUL M. TYLER. *Sci. Amer.*, **160**, 19–21 (1939).—T. reviews progress in the United States since 1912 in discovering new sources of minerals such as potash, new methods of separating minerals such as phosphates, and new uses for previously unwanted by-products such as scrap mica. W.D.F.

Mineralization from the Mötschlachgraben (graywacke zone). L. HAUSER AND F. SCHWARZ. *Berg- & Hüttenmänn. Monatshefte Montan. Hochschule Leoben*, **86** [10] 246–49 (1938).—The mineralogy, petrography, and geology of the Bruck-Leoben (Austria) district is explained. The chemical reactions which have formed the minerals can be expressed by the following scheme:

$$Al_2O_3\cdot 2SiO_2\cdot 2H_2O + 3MgO \rightarrow \underbrace{3MgO\cdot 2SiO_2\cdot 2H_2O}_{\text{kaolinite-serpentine}} + Al_2O_3$$

$$Al_2O_3\cdot 4SiO_2\cdot H_2O\cdot x\ \text{aq.} + 3MgO \rightarrow \underbrace{3MgO\cdot 2SiO_2\cdot 2H_2O}_{\text{montmorillonite-serpentine}} + 2SiO_2$$

$$n Al_2O_3\cdot m SiO_2\cdot x H_2O + 2MgO \rightarrow \underbrace{2MgO\cdot Al_2O_3\cdot SiO_2\cdot 2H_2O}_{\text{allophanton-amesite}} + (n-1)Al_2O_3\cdot(m-1)SiO_2\cdot(x-2)H_2O$$

M.H.

Mineralogical problems of crystal chemistry. PAUL NIGGLI. *Der feste Körper*, **1938**, pp. 1–23; *Chem. Abs.*, **33**, 448 (1939).—N. discusses crystal structures of minerals, the determining factors in lattice types, structure principles, and the relation between structure and outer morphology of growing crystals.

Models to aid in visualizing the optical properties of crystals. H. T. U. SMITH. *Amer. Mineralogist*, **23** [10] 629–43 (1938). F.J.Z.

Natural sources of uranium. A. ESME. *Argile*, No. 189, pp. 5–9 (1938).—Uranium oxides and uranates are used in ceramics for colorants, in glazes, and for luminescent enamels. Uranium has an atomic weight of 92 and exists in nature in the following forms: (*1*) *Oxides and hydroxides:* (*a*) pitchblende or uranite (U_3O_8), the principal mineral for uranium and radium; it has the form of a microcrystalline or amorphous mass with a black luster, is resinous, and is rarely in the form of crystals of the cubic system; (*b*) bröggerite and cleveite, Norwegian pitchblendes containing thorium; (*c*) nivenite, an American variety; (*d*) becquerelite ($UO_3\cdot 2H_2O$), schoepite ($UO_3\cdot 2H_2O$), janthenite ($2UO_3\cdot 7H_2O$), hydroxides from the Belgian Congo. (*2*) *Uranates*: (*a*) curite ($5UO_3\cdot 2PbO\cdot 2H_2O$); (*b*) fourmarierite ($4UO_3\cdot PbO\cdot 5H_2O$); (*c*) kasolite ($3SiO_2\cdot 3UO_3\cdot 3PbO\cdot 4H_2O$); (*d*) gummite (or halloysite) or eliasite ($SiO_2\cdot 3UO_3(Pb,Ca,Ba)O\cdot 6H_2O$), a silicouranate of lead, calcium, and barium; it is found in St. Joachimsthal, Johanngeorgenstadt, Saxony, and the U. S. and is an alteration product of pitchblende which it generally accompanies; (*e*) uranosphaerite ($U_2O_7(BiO)_2\cdot 3H_2O$), a uranate of bismuthyl found at Schneeberg, Saxony. (*3*) *Carbonates:* (*a*) rutherfordite ($CO_3\cdot UO_3$); (*b*) uranothallite ($(CO_3)_4U\cdot Ca_2\cdot 10H_2O$); (*c*) liebigite ($(CO_3)_3UO_2Ca\cdot 20H_2O$). (*4*) *Silicates:* (*a*) uranophane or uranotil ($2SiO_2\cdot 2UO_3\cdot CaO\cdot 4H_2O$), of interest in ceramics; (*b*) soddite or chinkolobwite ($5SiO_2\cdot 12UO_3\cdot 14H_2O$); (*c*) sklowskite ($2SiO_2\cdot 2UO_3MgO\cdot 7H_2O$). (*5*) *Phosphates:* (*a*) uranite or autunite ($(PO_4)_2(UO_2)_2Ca\cdot 8H_2O$); (*b*) chalcolite or torbernite ($(PO_4)_2(UO_2)_2Cu\cdot 8H_2O$), crystallizing in the quadratic system in crystals or lamellas of a green color; other uranyl phosphates are named. (*6*) *Sulfates:* double sulfates of uranyl and of calcium or of copper. (*7*) *Arsenates:* troegerite ($(AsO_4)_2(UO_2)_3\cdot 12H_2O$) and others. (*8*) *Rare elements:* carnotite, a yellow or greenish vanadate of uranyl and hydrated potassium ($2(VO_4)\text{-}UO_2K\cdot 3H_2O$) found in Colorado and Utah (also Australia and Madagascar); it contains radium and vanadium, while uranium is a valuable by-product. A series of vanadates, niobates, tantalates, and titanates of rare earths contains uranium. Deposits are located in Echo Bay (Canada), St. Joachimsthal (Bohemia, now a German possession), Guarda and Viseu (Portugal) Colorado and Utah, the Belgian Congo, Madagascar, Argentina, Cornwall (England), and Autun (France). The history of uranium is closely connected with that of radium, as all uranium minerals contain radium in the ratio of 1 part radium to 3 million parts uranium maximum. The production and price of uranium have been conditioned by new discoveries of radium deposits. With the work of Curie-Joliot on artificial radium, the price of uranium may eventually rise. M.V.C.

New deposit of corundum-dumortierite in central Kazakhstan. K. I. ASTASHENKO. *Razvedka Nedr*, **8** [3] 3–6 (1938); *Chem. Abs.*, **32**, 7374 (1938).—The ore contains about 70 to 85% of corundum, and the andalusite-dumortierite ore contains about 50 to 71% of dumortierite, 20 to 25% of quartz, and 5 to 10% of andalusite.

New size limits for silt and clay. HENRY G. KNIGHT. *Soil Sci. Soc. Amer., Proc.*, **2**, 592 (1937); *Chem. Abs.*, **32**, 8055 (1938).—Since Jan. 1, 1938, reports of the U. S. Bureau of Chemistry and Soils indicate particles less than 2 μ as clay and those 2 to 50 μ as silt. The fraction below 5 μ has also been determined to correlate future with past data. No change was made in the classification between 50 μ and 2 mm. Other changes permit reporting data under either the former American or the International systems of mechanical analysis.

Oil from shale. ANON. *Times Trade & Eng.*, **44** [899] 39 (1939).—Improved trading in the Scottish shale-oil industry in 1938 and new developments promise to place the industry on a very prosperous footing. Oil produced from shale can be made specially suitable for Diesel engines. The increased trade has led to further developments in the mining of shale and the refining of oil. The price of oil and other products was slightly reduced in 1938. A.B.S.

Oxidation-reduction potentials in soils. AMAR NATH PURI AND ANAND SARUP. *Soil Sci.*, **46** [4] 323–29 (1938).—The so-called oxidation-reduction potential (E_h) in soils is shown to be a fundamental property of all colloidal substances which furnish ionic micelles and behave as acidoids. The relation between p_H and E_h in soils is so perfect that the measurement of p_H should suffice for all practical purposes. G.R.S.

Petrological studies in the Harlech grit series of Merionethshire: I, Metamorphic changes in mudstones of the manganese shale group. A. W. WOODLAND. *Geol. Mag.*, **75**, 366–82 (1938).—Normal mudstone consists of quartz, dialogite, chlorite, sericite, garnet, magnetite, and sometimes tourmaline. Other types contain biotite in addition, are composed essentially of garnet and quartz, or have calcite, muscovite, and chlorite. The changes were made by low-grade regional metamorphism. **II, Petrography and petrology of grits.** *Ibid.*, pp. 440–54.—The coarse grit is mainly quartz of about 1 mm. grain size, with some feldspar, garnet, chlorite, and sericite. Heavy minerals found were zircon, garnet, tourmaline, anatase, rutile, epidote, enstatite, diopside, biotite, sillimanite, apatite, ilmenite, hematite, magnetite, pyrite, and chlorite. These are described and illustrated. **III, Development of pyrite in grits and mudstones.** *Ibid.*, pp. 529–39.—Pyrite is always surrounded by a zone of minerals formed there. One type has chlorite and chalcedony,

sometimes forming a fibrous intergrowth; sometimes magnetite, alone or with siderite, is also present. After the consolidation of the rock, the crystallizing pyrite (from FeS) contracted and left an opening and some excess iron which formed the magnetite. Circulating solutions deposited the others. W.D.F.

Petrology of Barnavave, Carlingford, I. F. S.: III, Hybrids from the eastern and southeastern slopes of Barnavave Mountain. S. R. NOCKOLDS. *Geol. Mag.*, **75**, 469–79 (1938).—Normal eucrite found here consists of a diallagic pyroxene and bytownite, with sometimes a little rhombic pyroxene. In the hybrid rocks, the pyroxenes show zoning and the feldspar is andesine almost completely sericitized. W.D.F.

Physical chemistry of clays used in papermaking. C. G. ALBERT. *Verre & Silicates Ind.*, **9** [34] 389–90 (1938).—A. presents an explanation of the colloidal chemistry and surface phenomena of ionization and adsorption involved in the behavior of clays and their application to the manufacture of paper. M.V.C.

Rapid determination of organic carbon in soil. E. M. EMMERT. *Soil Sci.*, **46** [5] 397–400 (1938).—The soil sample (0.25 to 2 g.) is heated strongly on a hot plate with 25 cc. of 50% (by volume) sulfuric acid in a 200 cc. Erlenmeyer flask until foaming ceases and the acid starts to condense on the sides of the flask. The cooled solution is made up to 25 or 50 cc. (depending on the C content) with 50% sulfuric acid. When the supernatant liquid is clear, it is compared with a standard in a colorimeter. G.R.S.

Silica sands of Ottawa. ANON. *Nat. Glass Budget*, **52** [50] 6, 16–17 (1937).—The history, development, hydraulic mining, and refining of Ottawa glass sand are described and illustrated. H.E.S.

Status of hornblende in low-grade metamorphic zones of green schists. C. E. TILLEY. *Geol. Mag.*, **75**, 497–511 (1938).—The Green Beds of the Highlands, originally sedimentary, have hornblende with a brownish green core of different composition than the colorless to pale green shell. This is due to the recrystallization of detrital hornblende. The green schists of the Start area, South Devon, originally basalt, have aluminous prochlorite and actinolite, together with epidote, albite, and sphene. Analyses of the rocks and some of the minerals are given and these analyses are plotted on diagrams. From these, the reactions necessary in the transformation are found. W.D.F.

Structures of kaolin and talc-pyrophyllite hydrates and their bearing on water sorption of the clays. STERLING B. HENDRICKS AND MERRILL E. JEFFERSON. *Amer. Mineralogist*, **23** [12] 863–75 (1938).—Vermiculites, montmorillonite, and hydrated halloysite contain layers of water molecules joined into extended hexagonal nets. The peculiar water sorptive properties of clays are considered to arise from the formation of successive layers of this type over the surfaces. F.J.Z.

Theory explaining the relation of soil-water ratios to p_H values. CLARK M. KEATON. *Soil Sci.*, **46** [3] 259–65 (1938).—The determination of the p_H values of several soils at different soil-water ratios ranging from a ratio of 1:10 to approximately normal moisture capacity, shows that the condition under which the soil reaction is determined by the use of a glass electrode has a pronounced influence on the p_H value obtained. In acid soils the minimum p_H value occurs when the soil-water ratio is at the point of the water-holding capacity of the soil. A further reduction in the soil moisture content results in increased p_H values because the proportion of metallic cations to hydrogen ions is low enough to produce a counteraction of the Debye-Hückel activity effect by the effect of preferential dissociation. In the more alkaline soils, the proportion of metallic cations is much higher than that in acid soils; the "activity effect," therefore, overshadows the effect of preferential dissociation, with the result that a continued decrease in p_H values takes place with decreasing moisture content. 10 references. G.R.S.

Thermoluminescence and its application for the control of feldspars in ceramic industry. MAURICE DÉRIBÉRÉ. *Argile*, No. 188, pp. 5–11 (1938).—The term "luminescence" is applied to that property of certain substances to emit light without undergoing a thermic transformation. Besides the phenomenon of luminescence known as fluorescence which is produced by Wood's light, there are other luminescence phenomena of practical interest in industry: (1) Photoluminescence is produced if the activating agent is luminous energy (X-rays, cathode rays, ultra-violet rays, and black or Wood's light). Photoluminescence is divided into two types: fluorescence (instantaneous) and phosphorescence (gradual restoration). (2) Chemical luminescence is produced if the activating agent is a chemical process, an example of which is the oxidation of phosphorus in the air. (3) Biochemical luminescence is produced by a biological process and is seen in glow worms, fireflies, pyrophorus, fungus, or luminous microörganisms. (4) Electroluminescence is produced by electrical excitation. (5) Galvanoluminescence is caused by electrochemical excitation. (6) Triboluminescence is produced mechanically. (7) Thermoluminescence is brought about by heating and cryoluminescence by cooling (M. Déribéré, Practical Application of Luminescence: Vol. 1, Dunod, Paris, 1938). Thermoluminescence is much less studied than photoluminescence, but it is a valuable means of identifying substances in mineralogy, *e.g.*, distinguishing between orthose or albite and other feldspars; it is used for evaluating the orthose content of a crushed rock by the intensity of the luminescence. When certain bodies are heated they emit a luminescence which is a characteristic identification of that body or a luminous element contained in it. Thermoluminescence is a luminescent emission of a body which has been brought from its metastable state to an active state from which it returns to the original state by restoring the accumulated energy in the form of a luminous radiation. Thermoluminescence of bodies with this property is produced by heating them progressively from 15° to 500° in 5 min. (the laboratory electric kiln gives good results) in a dark chamber; the rays are observed by the eye, a photoelectric cell which registers the intensity, a photographic plate from which the quantity of emissions is calculated, or by a spectrograph which analyzes. It is usually unnecessary to heat a body to redness to observe luminescence. Feldspars and feldspathoids show interesting thermoluminescences: albite, $Al_2Na_2(Si_3O_8)_2$, gives a greenish thermoluminescence; orthose, $Al_2K_2(Si_3O_8)_2$, gives blue thermoluminescence (with the exception of New Jersey microclines and certain feldspathoids such as hackmannite). M.V.C.

Thixotropy of mineral powders of microscopic sizes. HELMUTH G. F. WINKLER. *Kolloid-Beihefte*, **48**, 341–76 (1938).—Thixotropy is a sol-gel transformation occurring at constant temperature in submicroscopic and microscopic systems. A system in the sol state, containing slight amounts of electrolytes, will coagulate on standing. Mechanical disturbance, such as shaking or stirring, will liquefy the mixture, but after a certain time of rest the system will return to its former (congealed) state. The degree of thixotropy was qualitatively and quantitatively determined on a number of mineral powders of definite grain sizes mixed with water and thirteen other organic liquids (benzene, carbon tetrachloride, xylol, acetone, methyl alcohol, ethyl alcohol, etc.). It was found that all anisometric sheetlike or rod-shaped structures such as kaolin, halloysite, muscovite, graphite, and tremolite showed a high degree of thixotropy when mixed with water. The nearly isometric particles of quartz, feldspar, and fluorspar of the same grain size (20 to 2 μ r.) exhibited no thixotropy in water, but the same materials of much finer grain size (feldspar 3.2 to 0.5 μ r., quartz 1.8 to 0.5 μ r.) showed a slight thixotropic behavior. In nonaqueous liquids such as benzol, powdered window glass, ground flint, powdered fused quartz, and feldspar formed thixotropy and showed good plasticity. Thixotropy and plasticity both require a fine grain size and the ability to adsorb sufficiently large liquid films. All substances, if sufficiently fine grained, develop thixotropy. Electrolytes are not necessary. 11 diagrams, 4 tables, 29 references. L.E.T.

Use of bleaching clays in water purification. PAUL WEIR. *Amer. Inst. Mining Met. Engrs. Tech. Pub.*, No.

1018; *Mining Tech.*, **3** [1] 10 pp. (1939).—Two types of bleaching clays are (1) fuller's earth, naturally active, occurring most frequently in the southeastern states; and (2) bentonite, activable by acid, most prevalent in the southwest. Fuller's earth is nonplastic, adsorbent, foliated, and nonswelling. Bentonite is waxy, slakes, is less adsorbent, and swells to a heavy gel. Their use (1) promotes a more rapid settling floc, to which it adds toughness and weight; (2) reduces or removes certain bad tastes and odors; (3) reduces organic coloring matter; and (4) exerts some zeolitic effect on many hard waters. The use of clay at Atlanta, Georgia, is described in detail. About 20 to 40 lb. per million gallons are used at a cost of a $^1/_2$¢/lb. Other cities using such clay are briefly mentioned.

W.D.F.

Weathering of potassium feldspar. Carl W. Correns and Wolf von Engelhardt. *Naturwissenschaften*, **26**, 137–38 (1938); *Chem. Abs.*, **32**, 8306 (1938).—Pulverized clear adularia pieces of a size smaller than 1 μ and those from 3 to 10 μ in size were treated for 6 months with solutions of p_H 0, 3, 6, 7, and 11 in ultrafiltration apparatus. The extract obtained was of ionic or similar dispersion; the rate of solution differed for the components SiO_2, Al_2O_3, and K_2O. Thus protective layers (0.05 μ [illegible]e) of the least soluble material are formed, and the rate [illegible]olution of the remainder is retarded. Eventually, comp[illegible]olution takes place, and there is no SiO_2 skeleton left and no colloidal solution of SiO_2 or Al_2O_3.

Working up of Grecian bauxites. C. Zenghelis. *Compt. Rend. 17me Congr. Chim. Ind.*, **1937**, pp. 635–38; *Chem. Abs.*, **32**, 7221 (1938).—Z. briefly describes and discusses Grecian bauxite deposits and their working at the present time.

BOOK AND SEPARATE PUBLICATION

Annual report of the Nonmetals Division, fiscal year 1938. Oliver Ralston, et al. *U. S. Bur. Mines Repts. Investigations*, No. 3427, 38 pp. Free. R. covers the division's work on potash investigations, calcination and hydration of lime, and production of lightweight aggregates from slate quarry and mill wastes; utilization of opaline silica for production of silica brick; plastic flow and plasticity of mineral dispersions; properties of olivine refractories and use of olivine as a foundry sand; quantitative spectroscopy, beneficiation of an Alabama kaolin, and coal investigations; cracking of steel by boiler water; float and sink fractionation of low-phosphorus ferruginous sandstone; flotation and agglomeration processes; and electrostatic concentration of minerals. R.A.H.

Manual of Sedimentary Petrography: I, Sampling, Preparation for Analysis, Mechanical Analysis, and Statistical Analysis. W. C. Krumbein. **II, Shape Analysis, Mineralogical Analysis, Chemical Analysis, and Mass Properties.** F. J. Pettijohn. D. Appleton-Century Co., Inc., New York, 1938. Century Earth Science Series. Edited by Kirtley F. Mather. 550 pp., 265 figs., 53 tables. Price $6.50. This book deals with methods, apparatus, and data analyses of sedimentary petrography and sedimentary petrology. If the authors seem to have one purpose of greater moment than others it is to develop ability and means of obtaining and exactly interpreting analytical data. Discussions of methods and refinement in technique are directed to data interpretation. They have compiled information from many literature sources and give a voluminous bibliography. Principles and concepts of mechanical, chemical, and optical analysis are carried through the several chapters. Graphic presentation of data and statistical analysis are exhaustively treated. For anyone who is making physical, chemical, and mineralogical studies of clays and mineral powders, these two treatises are of value. It is one thing to collect data and quite another to assemble the data so as to enable them to be fully interpreted. The graphic and mathematical treatment of data are presented in a very readable way. This book is not a science treatise as it is a compilation of laboratory methods and a description of procedures.

R. C. Purdy

Chemistry and Physics

Chemical composition of magnetoplumbite. Ragnar Blix. *Geol. Fören. Förh.*, **59**, 300–302 (1937); *Chem. Abs.*, **32**, 1616 (1938).—The mineral magnetoplumbite from Långban, originally described by Aminoff, has been subjected to new analyses. From Aminoff's figures, reproduced in the article, B. has devised a new method. By repeated crushing and magnetic separation, B. reduced the mica content to 1.19%. By analysis of this magnetoplumbite containing 1.19% mica and an analysis of mica containing 4.36% magnetoplumbite, he obtained data for mica recalculated into pure mineral and finally the following figures for magnetoplumbite recalculated into pure mineral: H_2O 0.08, TiO_2 4.14, PbO 20.02, Al_2O_3 1.86, Cr_2O_3 0.25, Fe_2O_3 52.22, MnO 19.25, MgO 0.15, CaO 0.28, O 1.175, sum 100%. From this, B. calculated the formula for the mineral as probably $RO \cdot (R_2O_3)_6$.

Chromium determination in chromite and ferrochrome. Yu. I. Usatenko. *Zavodskaya Lab.*, **7**, 532–34 (1938).—U. developed a more precise method of determining chromium by dissolving the sample in a mixture of concentrated sulfuric and phosphoric acids. He established the effect of $AgNO_3$, $(NH_4)_2S_2O_8$, and the acidity on the velocity of oxidation of trivalent chromium to six-valent chromium.

P.B. & E.S.

Cone-fusion study of mixtures of zirconium silicate, silica, and alumina. Robert F. Rea. *Jour. Amer. Ceram. Soc.*, **22** [3] 95–96 (1939).

Determination of manganese in silicates. Manganese problem in the analysis of silicates: IV, Supplementary notes and a new method of manganese oxidation. Oskar Hackl. *Z. Anal. Chem.*, **112** [5–6] 174–79 (1938).—Platinum foil, but not platinum black, sponge, gauze, or platinized silica, can be used to catalyze the oxidation of Mn to MnO_4' by $(NH_4)_2S_2O_8$ and H_2SO_4. The solution must be free from Cl', traces of which cause incomplete oxidation. This method could be applied to the colorimetric determination of traces of Cl'. The reaction is much less sensitive to the presence of F'. Any Ti present is oxidized with the Mn^v, interfering with the colorimetric test. Addition of sufficient H_3SO_4 to suppress this oxidation also prevents complete oxidation of Mn^v. See "Manganese—," *Ceram. Abs.*, **16** [11] 355 (1937). E.J.V.

Determination of metalline iron in presence of its oxides in alumina cements. V. T. Illuminskaya. *Zavodskaya Lab.*, **7**, 609–10 (1938).—I. experimentally checked the electrolytic sulfate, mercuric bichloride, iodine, and bromine methods. All methods proved to be inadequate for analyses of alumina cements, with the exception of perhaps the Rooney and Shapleton modification of the iodine method (not checked by I.) and the Treje and Benedicks electrolytic method which needs further elaboration.

P.B. & E.S.

Determination of quartz by thermal differential analysis. F. Trombe. *Compt. Rend.*, **207** [23] 1111–13 (1938).—T. describes an exact method for the identification and quantitative determination of quartz in a powder mixture by a precise thermal analysis of the α–β transformation. The behavior of quartz is entirely different from that of silica, especially in the vitreous state. An example of a determination is given in detail. Five references. M.H.

Determination of silica in quartzites by evaporation with hydrofluoric acid. T. Kvist. *Z. Anal. Chem.*, **114** [1–2] 21–26 (1938).—In the routine determination of silica in quartzites, evaporation with hydrofluoric acid in the presence of sulfuric acid does not give correct values, but one evaporation with hydrofluoric acid alone gives a result that is apparently correct. Repeated evaporations in order to reach constant weight give results which are too high. E.J.V.

Direct determination of aluminum earths, *e.g.*, bauxite.

P. URECH. *Z. Anal. Chem.*, **111** [9–10] 337–42 (1938).—The chief difficulty in the analysis of an ore of aluminum, such as bauxite, lies in the determination of Fe_2O_3, Al_2O_3, and TiO_2. A convenient method of analysis consists in adding 2 g. of tartaric acid to the sulfate solution of 0.1 g. of the three oxides, reducing the slightly acid solution with H_2S, and adding more NH_4OH and more H_2S. This causes precipitation of FeS which can be filtered off and analyzed in any conventional way. The addition of 10 g. malonic acid and 1 g. NaOAc to the solution containing Ti and Al prevents the precipitation of Al by 8-hydroxyquinoline if the solution is first neutralized with ammonia and then made faintly acid with 1 to 2 ml. of AcOH; Ti, however, precipitates under these conditions. The Ti-oxine precipitate can be dried and weighed without ignition. The addition of more oxine and ammonia in slight excess to the filtrate from the Ti precipitate causes the precipitation of Al hydroxyquinolate. This can be dried at 130° and weighed or ignited with oxalic acid to Al_2O_3. The results obtained in the analysis of synthetic mixtures showed good agreement. A sample of bauxite contained 61.33% Al by difference and 61.23 to 61.34% by oxine precipitation.
E.J.V.

Forces which govern the atomic nucleus. M. A. TUVE. *Sci. Monthly*, **47** [4] 344–63 (1938).—T. discusses the nature of the forces acting deep within the atom and describes the construction and design of large-scale apparatus for studying nuclear physics and magnetism. Illustrated.
H.E.S.

Fusion point of coal ash. L. BRO. *Chaleur & Ind.*, **19** [223] 583–89 (1938).—B. describes the behavior of certain coal ashes under all atmospheric conditions represented by a surface defined by two curves—one for oxidizing and one for semireducing conditions—showing the amount of deformation of ash samples at increasing temperatures. Samples of two coal ashes were examined by reflected light under magnifications of 6 to 60 diameters after heating at temperatures of 1000° to 1425°C. No definite point of fusion existed, there being a range of 100° to 300°. The influences of various oxides are discussed. 19 photomicrographs.
V.D.F.

Generation of reference frequencies. L. A. MEACHAM. *Bell Lab. Record*, **17** [5] 138–40 (1939).—M. discusses a system for the production of precise reference frequencies suitable for controlling the adjustment of quartz crystals and for other uses. Illustrated.
P.S.D.

Microdetermination of lead by means of electrolysis and dithizone. H. MÜLLER. *Z. Anal. Chem.*, **113** [5–6] 161–82 (1938).—M. investigates the dithizone method for determining lead. Study of the sensitiveness of the reagent toward oxidizing agents and the action of light, the difficulty of complete extraction of the lead, the effect of p_H, possible losses in washing with ammonia water and KCN solution, and the marked interferences due to the presence of cations such as Bi, Zn, Sn, and Tl reveals the possibility of introducing serious errors into the determination. A procedure for determining lead in the absence of Bi, Sn, Tl, and large amounts of Zn which minimizes these errors as far as possible is described. Data showing the effect of acid concentration, stirring, N oxides, etc., on the electrolytic method are also recorded and discussed. Cl' and PO_4'' must be absent, but, except in the case of large amounts of Bi, interference by cations is not serious. Details of a suitable procedure are given. When the colorimetric comparison using tetrabase is supplemented by an iodimetric titration the electrolytic method extends from 5 to 5000 μg. lead. The relative merits of the two methods are compared; the electrolytic method is preferred for the determination of lead in biological material.
E.J.V.

Nature of solutions and their behavior under high pressures. R. E. GIBSON. *Sci. Monthly*, **46** [2] 103–19 (1938).—G. explains and illustrates a technique for studying the physical chemistry of silicates under high pressure and temperatures. See *Ceram. Abs.*, **16** [8] 260 (1937).
H.E.S.

Separation of magnesium from sodium and potassium with triton B. TADEUSZ KROKOVSKI. *Z. Anal. Chem.*, 112 [5–6] 183–86 (1938).—In the absence of NH_4', Mg'' can be precipitated quantitatively as $Mg(OH)_2$ by the addition of 50% excess of the base triton B (I), thus permitting its separation from Na′ and K′. Further addition of 9 cc. of 2.5 *N* I /1 g. NH_4Cl present causes quantitative precipitation of $Mg(OH)_2$, even in the presence of NH_4'.
E.J.V.

Shortening of the evaporating time of the silicon determination method according to Otis-Handy. H. FUCHSHUBER. *Chem.-Ztg.*, **62** [82] 743 (1938).—The addition of ethyl alcohol during the evaporation of the acidic silicon solution prevents spattering and the evaporation is thus hastened. Alcohol (96%) free from impurities is added until the solution stops foaming; 10 cc. are added in excess. The procedure is completed in the usual manner.
D.A.B.

Significance of the ability of hydrochloric acid to attack clay. W. L. E. DE KEYSER. *Natuurw. Tijdschr.*, **20**, 137–41 (1938); *Chem. Abs.*, **32**, 6819 (1938).—A modification of the pipet sedimentation method of Vinther, Heikel, and Lasson (*Ceram. Abs.*, **12** [12] 434 (1933)) was used to determine the particle size of various kinds of clays. The amount of Al_2O_3 extracted by approximately 1:7HCl in 3 hr. was also determined, and K. found that the percentage of Al_2O_3 (calculated on the total weight of sample) was roughly proportional to the percentage of particles with diameters less than 0.5 μ. The method is suggested as a possible means for the determination of allophane.

Ternary and quaternary systems alkali oxide–CaO–SiO_2–CO_2: I. CARL KRÖGER. Translated in *Glass Ind.*, **19** [9] 341–44; [10] 381–86 (1938); see *Ceram. Abs.*, **17** [6] 234 (1938).
E.J.V.

Use of X-rays in the ceramic industry. POL DUWEZ. *Verre & Silicates Ind.*, **9** [35] 402–403 (1938).—The following principles can be used in ceramics: (1) the spectroradiograph of a crystalline powder gives, because of the diffraction of the X-rays, a spectrum of characteristic diffraction which permits the identification of the crystal constituent without ambiguity; (2) the spectroradiograph of a powder containing *n* kinds of crystals gives *n* superposed spectrums, enough of whose most characteristic rays are visible and permit the qualitative determination of the constituents; (3) the comparison of the blackening of the photograph from different spectral rays indicates the intensity of these rays and the content of the different bodies, and, under certain conditions, this readily permits a certain semiquantitative analysis, *e.g.*, the determination of the free quartz content of a clay. In certain cases a spectrum can be obtained by reflection on a surface of the specimen, but since the X-rays do not penetrate deeply, only the glaze can be studied; being vitreous, it does not give a spectrum with sharp rays. In regard to porosity, D. cites a method related to radiography: a radioactive solution is absorbed and the proportion of the *demi-vie* of the substance lining the open pores permits the determination of the interior surface of the latter. Combined with the absorption method, this method gives an idea of the ratio of surface to volume of pores and their dimensions.
M.V.C.

Volumetric determination of fluoride and silicofluoride ions. W. GEFFCKEN AND H. HAMANN. *Z. Anal. Chem.*, **114** [1–2] 15–21 (1938).—F' and SiF_6'' are determined with an accuracy of 1% by acidifying the solution with a known excess of HCl and titrating with KOH and K_2SiO_3, using suitable indicators. The method is based on the reaction $6F' + SiO_2 + 2H_2O \rightleftharpoons SiF_6'' + 4OH'$.
E.J.V.

X-ray studies on magnetoplumbite, $PbO \cdot 6Fe_2O_3$, and other substances resembling beta-alumina, $Na_2O \cdot 11Al_2O_3$. VOLRATH ADELSKÖLD. *Arkiv Kemi Mineral. Geol.*, **12A** [29] 9 pp. (1938); *Chem. Abs.*, **32**, 8989 (1938).—A complete structure determination of magnetoplumbite shows a close similarity to beta-alumina, but not identity, owing to a difference in cell content. The only admissible composition is $PbO \cdot 6Fe_2O_3$, contradicting earlier analytical data ("Chemical composition—," this issue). The hexagonal unit, with axes $a = 5.877$, $c = 23.02$ Å, space group D_{3d}^3, contains $2(PbO \cdot 6Fe_2O_3)$. Axes of 6 compounds having this structure and 4 compounds having the beta-

alumina structure are tabulated; it appears that, in the former group, Ca ferrite and, in the latter group, Li, Na, and Cs ferrites do not exist.

BOOK

First Report on Viscosity and Plasticity prepared by the Committee for the Study of Viscosity of the Academy of Sciences at Amsterdam. N. V. Noord-Hollandsche Uitgevers-Mij., Amsterdam, 1935. Price 10 fl. *Verhandel. Akad. Wetenschappen Amsterdam, Afdeel. Natuurkunde*, [Sect. 1] **15** [3] viii + 256 pp. (1935); reviewed in *Nature*, **136** [3444] 697–99 (1935).—The report deals with the measurement and physical significance of the different types of slow flow occurring in liquids and solids, excluding vortex motion. J.L.G.

PATENTS

Manufacture and production of chrome yellow. G. W. JOHNSON (I. G. Farbenind. A.-G.). Brit. 498,487, Jan. 18, 1939 (July 9, 1937).

Producing caustic borate products. C. F. RITCHIE AND L. G. BLACK (American Potash & Chemical Corp.). U. S. 2,146,093, Feb. 7, 1939 (Feb. 17, 1936).

Producing high-grade zinc oxide. M. M. PEARLMAN (Superior Zinc Corp.). U. S. 2,147,379, Feb. 14, 1939 (Aug. 26, 1937).

Sodium sesquisilicate and mixtures including it and method of manufacturing. C. L. BAKER (Philadelphia Quartz Co.). U. S. 2,145,749, Jan. 31, 1939 (Nov. 12, 1934). In the preparation of definite crystalline hydrates of sodium sesquisilicate from silicate solutions containing more water and less Na_2O than is required to produce the final hydrate product, the process comprises evaporating excess water from such a silicate solution by heating it, the Na_2O present during the heating step being not substantially more than that corresponding to a molar ratio of $1Na_2O$ to $1SiO_2$, cooling the resulting solution to lower temperatures below its boiling point and below temperatures at which any extraneous hydrate is precipitated upon the addition of caustic soda, then adding caustic soda at the lower temperatures sufficient to produce a molar ratio of substantially $1^1/_2Na_2O$ to $1SiO_2$, and crystallizing the solution as a whole without exceeding the lower temperatures, thereby producing a hard and brittle product capable of being ground to a free-flowing, granular condition; the water content of the solution is adjusted to that of the final hydrate product prior to the crystallizing step.

General

Aluminum and silicosis. R. C. EMMONS AND CARL FRIES. *Amer. Mineralogist*, **23** [10] 654–60 (1938).—In the lung the harmful influence of silica is apparently at its peak when the silica is present as a colloid. The system is unable to handle it in this state. The chief conclusion is that the action of a protector, whether mineral or metallic, seems to be to collect this disperse silica into unit aggregates which may be removed by phagocytosis. F.J.Z.

Engineering students need more fundamental studies. ANON. *Science News Letter*, **34** [1] 7 (1938).—Less practical studies and more basic understanding of engineering principles are advocated. Too many short cuts are being taught instead of a proper understanding of the underlying principles of mathematics and physics on which all engineering is based. P.G.H.

Estimation of radiant heat exchange in boiler furnaces. G. A. ORROK AND N. C. ARTSAY. *Combustion*, **9** [10] 37–42 (1938).—The results and limitations of various theoretical and mathematical analyses are pointed out. With these as a background, certain modifications are suggested in the light of actual operating conditions, and simplified empirical expressions are offered. These are checked with the results of a large number of boiler tests; these results are appended. H.E.S.

Experimental fusing of diabase in shaft furnace. L. O. SARAPIN. *Mineral. Syr'e*, **12** [7–8] 57–63 (1937); abstracted in *Referat. Silikatliteratur*, **5** [4] 5109 (1938).—As shaft furnaces are superior to tank furnaces in their fusing power, S. attempted the fusing of diabase in a research shaft kiln (illustrated); at first, during fusing, the shaft became clogged with rock and the heating gases were forced back into the furnace with great loss in heat economy. A diabase from Onegasee with a composition 49.6 SiO_2, 5.0 MgO, 8.8 CaO, 18.9 Al_2O_3, 11.5 Fe_2O_3, 3.3 Na_2O, 0.8 K_2O, 2.0 TiO_2, and 0.1% SO_3 was used. Fusing time was shortest when lumps of diabase of 1 to 2 kg. were used. At 1300°, 90 kg. diabase required $5^1/_2$ hr. to melt; temperatures up to 1450° shortened the time. M.V.C.

Experimental reproduction of the so-called silicotic nodule. A. POLICARD. *Bull. Histol. Appl. Physiol. Path. Tech. Microscop.*, **15**, 67–76 (1938); *Chem. Abs.*, **32**, 8622 (1938).—Histological and histochemical studies were made of pathological tissue from the lungs of guinea pigs, rats, and rabbits which had inhaled quartz or chalcedony dust for 8 to 25 months. The fibrous changes produced in the lungs of these animals differed markedly from the fibrohyalin nodules found in human silicosis patients. P. concludes that the origin of human silicotic nodules can not as yet be definitely ascribed to silica itself.

Lead poisoning in the ceramic industry: I. H. LEHMANN AND M.-T. SCHULZE. *Ber. Deut. Keram. Ges.*, **19** [2] 38–46 (1938).—According to statistics compiled in 1936, lead poisoning accounts for about 60% of the occupational diseases caused by chemical substances. Preliminary experiments are described, of which the final objective is the determination of those lead silicates which are harmless to operatives. By arrangement with two hospitals, solubility determinations were made with natural stomach juices, as well as with 0.3% HCl, HAc, etc. Results were reported of tests of two glazes, A and B, with total lead contents of 20% and 22% and lead contents in the frit of 24% and 30%, respectively. In all the experiments, 10 g. of solid were taken to 100 cc. of acid or stomach juices, and the normal duration of the test was 10 days. The temperature was maintained at 36° to 37°C. Under these conditions and using stomach juice of acidity 60, *i.e.*, 100 cc. stomach juice requires 60 cc. *N*/10 caustic soda solution for titration, the two glazes gave up an average of 0.003% lead, *i.e.*, 0.03 mg. of lead was dissolved out of 1 g. of glaze powder. Under the same conditions, glaze A gave up 0.004% and glaze B 0.01% lead in *N*/10 HCl; with 4% HAc the corresponding figures were 6.5% and 13.1%. **II.** A. BRANDT. *Ibid.*, pp. 46–54.—B. presents a preliminary report on investigations to determine what quantities of lead are dangerous to health in general, what quantity of lead is taken up by the body when working with different glazes, and how the body reacts when lead is introduced (*a*) by the stomach and (*b*) via the lungs. The clinical aspect of lead poisoning is briefly outlined and works preventive methods are discussed. See *Ceram. Abs.*, **17** [11] 359 (1938). E.J.V.

Load distribution on boilers. Y. C. LU. *Combustion*, **9** [11] 27–30 (1938).—L. discusses the load distribution on boilers by the method of equal increments. The analysis endeavors to prove that incremental input curves should be plotted on the basis of dollar input instead of B.t.u. input which may show a false economy. H.E.S.

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